ENHANCED POLYELECTROLYTE MULTILAYERS FOR HIGHLY SELECTIVE MEMBRANES

FROM DENSIFICATION TO AQUAPORIN WATER CHANNELS

DENNIS M. REURINK

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Dennis Maik Reurink

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“If you want to build a ship, don’t drum up the men to gather wood, divide the work, and give orders. Instead, teach them to long for the endless immensity of the sea.”

Antoine de Saint-Exupéry (1900 – 1944)

French aviator and writer

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Chapter 1

Introduction

1.1 Motivation

Water, one of the most important substances in the world has always fascinated me. From rivers to seas to clouds to rain, the simple cycle of water which determines so many things. Countries that struggle with floods, droughts, or hurricanes, all so different but all have a common constant factor, water. The simplicity of the molecule consisting of two hydrogen and one oxygen atom is deceiving. Hydrogen, sitting on the places of the oxygen's p-orbitals makes a distinctive angle of around 104° that gives water its remarkable properties. We do not notice or think about it that often, but water is one of the substances that is an exception to the rule. Due to the angle of the hydrogen atoms, a strong dipole is present as well as the ability to form strong hydrogen bonds with itself. These properties mean, that the density of water is highest around 4°C , while its freezing temperature is 0°C . Therefore, ice (solid water) can float on liquid and, which creates the possibility, for example, for people to ice skate. Also, due to its high polarity, water is known as the universal solvent that can dissolve an abundance of materials, and this is where we membrane scientists play an important role.

The constant struggle of any separation scientist is to pay the penalty for de-mixing in order to separate substances from each other. This is the reason why desalination is thermodynamically limited to 1.03 kWh/m^3 (at 50% recovery) [1] since this is the minimal energy that needs to be paid in order to separate salt from water. In real modern desalination plants this number is higher where $3\text{--}3.5 \text{ kWh}$ of energy is needed to produce one cubic meter of fresh water from seawater. [2, 3] One can see it as a simple transaction, and it is the way the transaction is being performed that determines how efficient the final separation will be.

On one hand, it is a blessing that water can dissolve so many components, just look at our own bodies. On the other hand, everything that is present in the environment is partly dissolved in water, like salts that are present in lakes and seas either in low or high amounts. Consequently, everything that is being disposed of, thrown away, or flushed away by us will end up in our water ways. This improper waste disposal due to human activity causes contamination of our rivers, lakes, seas, and oceans with among many others (micro)plastics, micropollutants, and fertilizers.

In regions with a low amount of freshwater reserves, desalination is vital to ensure a constant clean supply of drinking water. In other places like the Netherlands, drinking water is extracted from the surface (rivers and lakes) or from ground water reserves. There are clear signs that surface waters near the coast become more salty due to the invasion of

seawater. Another emerging problem is the contamination of our drinking water reserves by micropollutants. These pollutants are a variety of molecules that include; antibiotics, pesticides, herbicides, hormones, medicines, plasticizers, and other man-made compounds.

The increasing amount of salt and contaminants like micropollutants should be removed from our water before it can be used as drinking water. In order to contribute to this overarching goal, this thesis investigates the development of new, more selective, and highly permeable water filtration membranes. These membranes are fabricated by the layer-by-layer technique of oppositely charged polyelectrolytes and the water selective aquaporin containing vesicles. The fundamental properties of these thin layers are studied and their separating properties in various membrane operations to obtain a deeper understanding of the separation processes.

1.2 Polyelectrolytes

First, a couple of definitions should be explained that will be used frequently in this thesis. Polyelectrolytes (PEs) are polymers that have a substantial portion of ionizable and/or ionic groups in their repeating unit. [4] A distinction is made between weak and strong PEs, where weak PEs are ionizable and strong PEs keep their charge over a broad pH range (roughly between pH 0 and 14). Subsequently, a different terminology is used for PEs bearing a negative and positive charges, namely a polyanion and polycation. There are also PEs that have both a negative and positive charge, those are called polyzwitterions [5] and polyampholytes [6]. Here, polyzwitterions have both charges on the repeating unit whereas polyampholytes contain both charges along the polymer chain, either symmetrical or asymmetrical. In **Figure 1.1**, the various types of polyelectrolytes are schematically shown and the mechanism of a weak polycation and polyanion is illustrated.

Many types of polyelectrolytes exist from natural to semi- and fully synthetic PEs. Semi-synthetic PEs are often chemically modified natural PEs. Among natural PEs, proteins are the most well-known, xanthan gum is an example of a semi-synthetic PE, and sulfonated polystyrene is a fully synthetic PE. [7] PEs are widely used in various fields from the food, cosmetics, textile, and paper industry to the pharmaceutical, medicine, and biomedicine industry. [8] In these fields, PEs are used as materials for coatings, as surfactants, in complexes for drug delivery, controlled swelling for optical devices, [9] and many more. Another field in which PEs are used is the field of membranes, using just a single PE layer or by using polyelectrolyte multilayers interfacial behavior of membranes can be altered and controlled.

Figure 1.1: Schematic of different polyelectrolytes; polycation, polyanion, polyzwitterion, and polyampholyte. The dissociation of weak polyelectrolytes is illustrated where the weak polybases are protonated below and weak polyacids are deprotonated above their pK_a value.

1.3 Polyelectrolyte multilayers

As explained in the previous sections, PEs are charged and this charge means that PEs can adsorb onto oppositely charged surfaces. The reason why these PEs adsorb is that there is a gain in entropy through the release of bound counterions from the PEs into the surrounding solution, this creates more degrees of freedom for the counterions, and therefore, more entropy is created for the whole system. [10] Subsequently, when a PE adsorbs onto the surface, the charges of the adsorbing PE neutralize the opposite charge of the surface, this is also known as charge compensation. However, the last layer of the adsorbing PE cannot neutralize the bulk anymore and will stay at the surface which will result in a reversal of the surface charge, also known as charge overcompensation. [11] Now that the surface charge has been reversed, a polyelectrolyte with an opposite charge can be adsorbed onto the 'new' surface. By repeating this process as shown in **Figure 1.2**,

a polyelectrolyte multilayer (PEM) can be formed when the two oppositely charged polyelectrolytes are adsorbed alternately for a desired number of cycles. [12, 13]

Figure 1.2: Alternating adsorption of two oppositely charged polyelectrolytes (a polycation and polyanion) on an hollow fiber support to form polyelectrolyte multilayers.

There are several key parameters to control the buildup of a PEM; ionic strength, [10] type of salt, [14] temperature, [15] pH, [16] type of polyelectrolyte, [17] molecular weight, [18] fabrication method, [19] and number of layers. From these parameters, ionic strength is a very important parameter that can be easily adjusted by changing the salt concentration of the deposition solutions. At low salt concentrations (≈ 5 to 50 mM), the charges of the adsorbed polyelectrolyte are compensated by the charges of the adsorbing polyelectrolyte, this is termed intrinsic charge compensation. When the salt concentration increases (>50 mM), counterions will start to compensate the charges of the polyelectrolytes in a higher amount, this is termed extrinsic charge compensation. Both intrinsic and extrinsic charge compensations are schematically illustrated in **Figure 1.3**. Between intrinsic and extrinsic charge compensation as shown in **Figure 1.3**, there will always be an equilibrium as depicted by **Equation 1.1**. For this reason, the intrinsic and extrinsic equilibrium can thus be shifted by simply changing the salt concentration of the coating solutions. [20]

Figure 1.3: Schematic representation of intrinsic and extrinsic charge compensation at low and high salt concentrations respectively. Adapted with permission from R. v. Klitzing [21].

Besides the salt concentration used during buildup, another very important factor is the type of polyelectrolyte used and the combination of the two polyelectrolytes that make up the final multilayer. Different combinations of PEs can result in wildly different PEMs, but also the final PE can influence properties like surface tension, hydration, and zeta potential (layer charge). When a PEM is built, the alternating built up results in an alternating reversible zeta potential [22, 23] and contact angle [24] (surface tension indicator), termed the odd-even effect. [25] In literature, PSS/PAH (poly(4-styrene sulfonate)/poly(allylamine)) and PSS/PDADMAC (PSS/poly(diallyldimethylammonium chloride)), multilayers from synthetic PEs, are by far the two most studied systems. Although it is only the polycation that differs in these two multilayers, the properties and characteristics are significantly different. For PSS/PAH, the swelling of the multilayer depending on the terminating layer, is around 20-30%, [26] whereas the swelling of a PSS/PDADMAC multilayer is higher at around 30-40%. [27] Moreover, the odd-even effect of both multilayers is different where the PSS/PDADMAC multilayer is more swollen when the multilayer is PDADMAC terminated and the PSS/PAH multilayer when terminated on PSS, as shown in **Figure 1.4** for PSS/PAH. Both effects are due to different mechanisms which dictate the polymer interactions within the multilayer. The mobility of PDADMAC is higher than that of PSS and is thus more able to penetrate the multilayer

during adsorption. For this reason, PDADMAC is in excess within the multilayer with respect to PSS, and therefore, more positive charge is present which subsequently swells the whole multilayer. [28] Because PSS is less mobile, the top multilayer becomes glassier when PSS adsorbs, thus blocking the adsorption toward more PSS. With PSS/PAH multilayer, the polycation is also in excess within the multilayer, however, the odd-even effect is shifted where the multilayer swells more when PSS is adsorbed, as seen in **Figure 1.4**, instead of the polycation. When PSS is adsorbed onto the multilayer, the PAH in the multilayer protonates creating an excess of positive charge causing swelling of the multilayer. [29, 30] During the adsorption of PAH, more positive charges are introduced deprotonating the PAH within the multilayer, lowering the overall charge and swelling.

Figure 1.4: For a PSS/PAH multilayer the swelling degree of the total multilayer as function of the number of layers where the odd layers (open square symbols) are PAH-terminated and even layers (solid circle symbols) are PSS-terminated layers. Image used with permission from Wong et al. [26]

Besides PSS/PDADMAC and PSS/PAH there are many more types of multilayers studied in literature, however, these two are the most commonly used and studied for the application of membranes. The advantage of using PEMs is that the coating process is very straightforward and independent of geometry, meaning that a coating can be easily applied on the inside of a hollow fiber support membrane. In the next section, PEM membranes

will be discussed in detail, with the different applications explained together with the types of multilayers and fabrication methods most commonly used.

1.4 Polyelectrolyte multilayer membranes

In the past two decades, lots of research has been conducted on modifying membranes by applying a PEM to increase membrane selectivity for better performances or hydrophilicity for antifouling. Moreover, a large part of the literature is focused on fabricating PEM coatings in order for them to function as a new type of separating layer. In the first membrane studies in the early 2000s, PEMs were investigated as separation layers for pervaporation, [31-33] ion exchange, [34] gas separation, [35] nanofiltration, [36] forward osmosis, [37, 38] and reverse osmosis [39, 40] applications as schematically shown in **Figure 1.5**.

Figure1.5: Schematic illustration of different membrane applications studied in literature using PEMs. Possible applications are in gas separation, pervaporation, ion exchange, nanofiltration, reverse and forward osmosis.

Narrowing the focus to the use of PEMs as a separation layer for nanofiltration and reverse osmosis applications, PEM membranes can be constructed by a couple of techniques where dynamic [41] and static coating (dip-coating) [36] are the most common. Using

different coating technique results in a different PEMs, from the two methods described, the latter is the most used. Another advantage is that by using dip-coating, most of the PEM literature is available in order to thoroughly understand and compare the PEM that is on top of the membrane. In order to fabricate a PEM, any type of support material can be used as long as there is a surface charge present. When a PEM is coated on a support, the odd-even effect can be used to differentiate between a so-called pore- and layer dominated regime. [42] In the pore-dominated regime, the PEM is still in the process of closing the pores of the support in which the PE that swells the most will result in a pore closure at a lower number of layers. On the contrary, the PE with a lower swelling causes a pore opening since the multilayer on the pore walls shrinks resulting in a pore opening. In the case of PSS/PDADMAC this will result in a lower permeability when the PEM is PDADMAC terminated (pore closure) and a higher permeability when terminated on PSS (pore opening). When the number of layers increases the multilayer will transition into the layer-dominated regime. Here, the phenomenon is reversed, where the lower swelling PE will cause a densification of the PEM and the higher swelling PE causes the PEM to have a more open structure. [42, 43] For the PSS/PDADMAC case this means that when the multilayer is PDADMAC terminated, the permeability is higher than a PSS terminated multilayer. Both the pore and layer dominated regimes are schematically depicted in **Figure 1.6** and the distinction of both regimes is important to understand, since only in the layer-dominated regime can a defect free separation layer be formed. Moreover, knowledge of the two regimes allows for optimization of the thickness of the PEM membrane.

Figure 1.6: Pore- and layer dominating regime of a PEM membrane schematically illustrated. Image adapted with permission from de Grooth et al. [42]

Continuing on discussing swelling of PEMs, a strong correlation can be drawn between PEM swelling and PEM membrane performance. It was already mentioned that PDADMAC PEMs in the layer dominated regime swell more than the PSS terminated multilayers, this is due to the higher swelling of PDADMAC. PDADMAC terminated multilayers show a higher sucrose flux which is directly linked to the swelling of the PEM density, and therefore, the PEM membrane performance. [44] In the same study, it was also shown that hyaluronic/chitosan (HA/CHI) multilayers have a four times higher swelling degree than PSS/PAH multilayers and this resulted in a 250 times higher sucrose flux. A major difference between PSS/PAH and HA/CHI multilayers is the charge density of the individual PEs. The higher the charge density of PEs, the higher the degree of ionic crosslinking density. For this reason, less PEM swelling will occur since the PEs are more tightly bound, and therefore, denser PEMs are fabricated that result in better membrane performances. [43, 45] In other words, when the number of ion pairs per total amount of carbon atoms increases per monomer unit, it is shown that ion permeation rates through PEMs are lower. [46] What these studies show is that the density of the PEM and thus the membrane performance is connected to the PEM swelling and the degree of (ionic) crosslinking within the PEMs.

An important aspect to consider is the physical and chemical stability of PEM membranes. When a sufficiently high molecular weight of PEs is used, the physical stability is high.

When all charges of a PE are ionically bonded to the surface, desorption is more difficult at higher molecular weights since a high number of charges need to unbind from the surface simultaneously. For this reason, a higher molecular weight results in higher physical stability of the PEMs. Another important factor is the chemical stability, especially stability toward hypochlorite – a commonly used membrane cleaning agent – is needed for membrane applications. Nucleophilic attack of the strong base on the commonly used polyamide based thin film composite (TFC) membranes results in fast degradation of the separating layer. A commonly used PE pair to build a PEM membrane for nanofiltration is PSS/PDADMAC, this PEM is buildup from two strong PEs. Here, PDADMAC has a quaternary amine which is not susceptible to the nucleophilic attack of hypochlorite. This means that a PSS/PDADMAC multilayer has a very high chemical stability up to 100,000 times higher than a polyamide based TFC membranes. [47] Furthermore, PSS/PAH membranes showed a 1000 times higher chemical stability than the standard polyamide based TFC membranes, although the primary amines are prone to nucleophilic attacks. [47] This opens the opportunity to study different types of PEMs knowing that a certain acceptable level of chemical stability is still maintained and thus the PEM membranes will be viable for commercial applications. Moreover, PEMs were developed for membranes to have a sacrificial layer to physically remove fouling. [48] In this process, the PEM can be removed together with the foulant by exposure to a certain pH and salt concentration. Subsequently, a new PEM can be constructed on top of the membrane support by simply flushing the membrane module with the right PE solutions.

PEM membranes for nanofiltration have various applications including the recovery of dyes at the textile industry, [49] fractionation of amino acids, [50] and anion selectivity toward fluoride for removal from drinking water, [51, 52] sulfate for descaling, [53, 54] and phosphate recovery from waste streams. [55] As well as anions, multivalent cation selectivity over monovalent cations can be obtained for magnesium and calcium, [56] other multivalent cations that are scale forming, [57] and even selectivity between different oxidation states of the same ion (e.g., iron) [58] can be achieved. PEM membranes are also very suitable for selectively removing certain types of ions due to the Donnan-exclusion mechanism. [36] In addition, these properties can be easily tuned with PEM membranes since a different terminating layer or different salt concentration used during buildup can already substantially change the ion retention behavior. [42] Continuing on the retention of solutes, significant efforts have been made to develop PEM membranes retaining micropollutants. Zwitterionic based PEMs in combination with PSS and PDADMAC have been studied and these show a typical Donnan-exclusion behavior

and low retentions toward neutral micropollutants. [36] Subsequently, PEMs based on weak PEs (PAA/PAH) have been studied and show overall high retentions independent of the micropollutant charge. [59]

Moving to PEM membranes studied for RO applications, numerous studies were performed to investigate whether PEM membranes are suitable for desalinating water. With desalination, monovalent ions (mainly NaCl) are separated from water and ideally the membrane is able to retain all salts at very high feed concentrations. The first studies used PEs with very high charge densities, namely poly(vinylamine) (PVA) and poly(vinyl sulfonate) (PVS) and obtained high NaCl retention, however, only after a huge number of 60 bilayers ([PVA/PVS]₆₀). [39, 40] Other studies used PAH and PAA with 120 bilayers [60] or just 10 bilayers after thermally crosslinking the amine and carboxylic acid of PAH and PAA. [61] Although these layers showed good retentions toward NaCl, this comes at a great loss in permeability since a high layer number is used.

FO membranes have been developed using PEMs as well, in these studies, PAH and PSS [37, 62] and other PEMs like PDADMAC/PSS and PEI/PSS [63] were used in order to construct NF like FO membranes with high water fluxes. Subsequently, studies were performed to improve membrane performance by the incorporating of particles [64] or by crosslinking the PEMs in order to densify the PEMs [38, 65, 66].

Like mentioned in the previous section, PEMs can be built on any sample geometry. This means that a defect free separating layers can easily be coated on either the inside or the outside of hollow fiber membrane capillaries, normally a tedious operation. Moreover, a hollow fiber configuration possesses many benefits over flat sheet membrane configurations, since the clogging potential is lowered because no spacers are needed. In addition, hollow fiber membranes can be backwashed using high pressures to remove fouling. For this reason, a hollow fiber geometry allows for a simpler process using less pretreatment steps for fouling prevention. [67] In the next section, the role of PEM membranes for nanofiltration and forward/reverse osmosis processes will be discussed in more detail.

1.5 Nanofiltration and forward/reverse osmosis – The role for polyelectrolyte multilayer membranes

RO, desalination, or hyperfiltration membranes are so dense that water can be desalinated up to high feed concentrations of salt. With these membranes, the ideal case is that only

water can permeate the membrane and all other solutes are rejected. The process of osmosis or FO is that water flows over a semipermeable membrane that rejects all solutes from a region which has a high water chemical potential (low solute concentration) to a region with low water chemical potential (high solute concentration). Water flows because there is a difference in solute concentration and therefore a difference in osmotic pressure, like schematically depicted in **Figure 1.7**. Forward osmosis is a technique that uses osmotic pressure to transport water from the feed side (or freshwater side) of the membrane to the draw side (or saltwater side) containing a higher solute concentration. RO, also illustrated in **Figure 1.7**, is a process in which the osmotic pressure is overcome by applying an external pressure that results in a flow of water from the salt water side to the fresh water side, desalinating water and up-concentrating salt in the salt water compartment.

Figure 1.7: Schematic images of the forward (left) and reverse (right) osmosis processes. At forward osmosis, a saltwater solution with a high osmotic pressure draws the water from the freshwater side to the saltwater side. In reverse osmosis, pressure is applied until the osmotic pressure is overcome, then water flows from the saltwater side to the freshwater side, desalinating the water from the saltwater compartment in the process.

For both RO and FO, good performing membranes based on polyamide TFC technology are already commercially applied. What role can PEM membranes fulfill in both processes? In order to answer this, a good understanding of the limitations of both processes and other closely related membrane processes like brackish water RO (BWRO) and NF should be made. For desalination membranes (for both FO and RO processes) it is known that an increase in selectivity is necessary instead of an increase in permeability.

[68] Like mentioned in the previous section, a numerous amount of studies have investigated how PEM membranes could be densified in order to perform as desalination membranes. PEMs can be a very good fit for RO because hollow fiber geometries can be used, increasing the surface-to-volume ratio, the selectivity can be easily tuned, and surface properties can be controlled.

Unfortunately, when salt concentrations in the feed increase, depending on the salt type, salt retention of a PEM membrane decreases rapidly. The aforementioned [PVA/PVS]₆₀ membranes [39] showed Na⁺ retentions above 90% for 1:10 and 1:100 diluted solutions of seawater, however, when pure seawater was used, NaCl retentions dropped to 55% and 75% at 20 and 40 bar of pressure respectively. The [PAH/PAA]₁₂₀ membrane [60] showed similar behavior where the initial retention at 2000 ppm of NaCl was 65% and dropped to 45% when a concentration of 35000 ppm was used. PDADMAC/PSS membranes show in general high divalent/monovalent ion selectivities, [57] but these membranes naturally also show a decrease in overall retention when feed salt concentrations increase. This can easily be explained since an increasing solute concentration will screen the membrane charge and weaken the Donnan–exclusion effect. [69] Moreover, increasing salt concentrations leads to increased swelling of NF membranes [70] and PEMs [20] increasing the effective pore size, and therefore, decreasing selectivity. Furthermore, the PEM desalination membranes developed have high salt rejection, however, the retention comes at the cost of very low permeability. The [PVA/PVS]₆₀, [PAH/PAA]₁₂₀, and the aforementioned [PAH/PAA]₂₀ thermally crosslinked PEMs [61] have permeabilities of 0.1, 0.38, and 0.35 L·m⁻²·h⁻¹·bar⁻¹ respectively, whereas modern commercial RO membranes can have water permeabilities of 1–3 L·m⁻²·h⁻¹·bar⁻¹ while these membranes maintain high ion retentions even at high salt concentrations. [71] This means that PEMs can be made very dense, but at a high cost of water permeability.

However, for low and moderate salt concentration like in BWRO or NF processes, PEM membranes can be a good option, especially because high selectivities toward certain solutes can be obtained. These selectivities can be obtained in combination with high water permeabilities since the PEMs do not need to be as dense as those needed for RO. Because for NF membranes, not only an increase in selectivity but also an increase in permeability is desirable since electrolyte rejections can be lower than for RO membranes. For this reason, an increase in permeability is desirable and leads to lower energy costs for NF membrane operation. Here, PEM membranes become a serious competitive candidate since PEM membranes can have high permeabilities and tunable rejection mechanisms depending on the type of multilayers used. Therefore, the perfect type of multilayer can be

designed to fit a specific separation process, e.g., either the removal of salt or micropollutants from aqueous solutions. Permeabilities of PEM membranes mentioned in this chapter are on the order of 5 to $15 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$, which are high permeabilities for NF membranes. For this reason, PEM membranes are a good fit for either BWRO or NF processes. Still, for both BWRO and NF selectivity is still a very important property, and therefore, it is worthwhile to study how overall selectivity and selectivity toward specific solutes can be increased.

1.6 Increasing selectivity of PEM membranes

To push PEM membranes from their highly successful application as NF membranes to applications such as FO, BWRO etc., it becomes important to increase selectivity by densifying the PEMs. However, to increase membrane selectivity can be a difficult undertaking, as explained in the previous sections. One way to increase selectivity is to decrease the degree of swelling by increasing the crosslink density by either changing the PEs to create more physical ionic crosslinking or by chemically crosslinking the multilayers. Both approaches have been studied extensively but a good correlation is missing between the PE structure, and therefore, ionic crosslinking and the subsequent effectiveness of chemical crosslinking. This is important since chemical crosslinking can make a PEM denser, but this may also come with a huge loss in permeability.

As mentioned earlier, PEMs usually have an excess of one of the two PEs that increases the amount of excess charge within the multilayer and thus its swelling and surface charge. An approach in order to control the surface charge and thus membrane performance where found in terminating PSS/PAH multilayers by PSS deposited at high salt concentrations. [53, 72] In these studies they showed that by terminating the multilayer with a PSS solution containing 2.5 M of salt, resulted in a higher negative surface charge, and therefore, higher sulfate (divalent anion) retentions. These studies already took a step in the direction of using high salt concentrations in order to influence the charge balance of a PEM. A next step is to anneal PEMs by salt or temperature in order to control and remove the excess PE within the multilayer. [73, 74] It is expected that by removing or compensating the excess PEs, results in a more stoichiometric multilayer that can result in a better performing membrane. However, annealing of PEMs has not been used yet for PEM membranes, and therefore, the understanding why and if annealing works for a membrane application is yet unknown. The subjects reviewed in this section are about changing the PEM to enhance membrane selectivity. In the next part, another approach is

discussed on how to increase the selectivity of PEMs by combining them with biomimetic membranes.

1.7 Combining biomimetic and PEM membranes

Another approach to accomplish an increased selectivity is inspired by membranes based on biological membranes like to ones present in cell walls, these membranes are also called biomimetic membranes. [75] In the walls of cells, the aquaporin protein is a water channel that selectively transports water molecules up to one billion water molecules per second per channel. An ultra-narrow and hydrophobic channel within the aquaporin protein ensures that water molecules are transported in a single file while rejecting all other kinds of solutes. [76] The high selectivity resulting from the channel, that is illustrated in **Figure 1.8**, is due to several factors including the size restriction (hourglass shape), [77] dipole orientation of the water molecules, [78] and charge repulsion. [79] Because of the selective nature of the aquaporin water channel, when incorporated in a membrane it could be quite a promising approach to increase selectivities and permeabilities in RO, FO, and even NF. [80, 81] For this reason, numerous studies have attempted to incorporate active aquaporin proteins into membranes for enhancing the performance.

Figure 1.8: Schematic illustration of the Aquaporin-1 protein reconstituted within a lipid bilayer where in A the dipole orientation is shown and in B and C a more detailed diagram how the water molecule is transported through the pore constriction. Image is used with permission from Murata et al. [77]

In order to maintain activity and proper stability of the aquaporin protein, reconstitution into phospholipid bilayers [82] or amphiphilic block copolymer layers should take place. [83] From the two layers, block copolymers show the highest chemical and physical

stability [84, 85] and layer thickness and protein permeability can be tuned. [86] In order to translate these layers into membranes two approaches have been studied; namely planar [87] and vesicular biomimetic structures. [80] The latter, however, is mechanically more robust and can be incorporated within an existing layer fabricating inherently defect-free layers. The incorporation of aquaporin incorporated vesicles or proteoliposomes/-polymersomes can be achieved via several approaches. The vesicles can be deposited on a porous substrate and then sealed by a dense polymeric protection layer formed by chemical crosslinking, [88] interfacial polymerization, [89-91] or by incorporation in PEMs. [92, 93] In all approaches, both the proteoliposomes/-polymersomes and the polymeric layer in which the vesicles are incorporated contribute to the final permeability and selectivity. Although these studies successfully incorporated these vesicles into the layers, a good quantitative study is lacking on the total adsorption into PEMs and the usage of various PEs.

1.8 The place for polyelectrolyte multilayers in literature

The strength of PEMs is their versatility and ease of deposition on any geometrically shaped surface; only a charged surface is needed. For this reason, the coating of membranes with PEMs is an easy task and opens a whole field for modifying membranes. A simple search for “*polyelectrolyte multilayer*” in the database of Scopus produces at the time of writing 3749 hits with the first papers published already in the 1970s. However, as shown in **Figure 1.9**, the amount of papers published on PEMs really took off after the publication of G. Decher [13] on the alternate deposition of PEMs. **Figure 1.9** also shows that the peak amount of publications was between 2005 and 2016 and that there seems to be a decline in publications for polyelectrolyte multilayers from 2016 onwards. The search term “*polyelectrolyte multilayer membrane*” follows in the beginning the same trend of polyelectrolyte multilayers hitting 694 results in the Scopus database at the time of writing. According to the data plotted in this figure, after 2005 a stable amount of publications about PEM membranes are being produced, which is roughly 20% of the total PEM publications. This means that the contribution of the membrane field is quite substantial to the overall PEM literature with an increasing share since the total amount of publications on polyelectrolyte multilayers decreases. This means that PEMs for the

application of membranes still hold a great potential with challenging fundamental and applied research questions.

Figure 1.9: Publications per year for the search term “polyelectrolyte multilayer” and “polyelectrolyte multilayer membranes” in the Scopus database at the time of writing.

1.9 Thesis outline

Coming to the end of the introduction, the question arises of where my four years research lies in this whole story. The main aim of this thesis is to create denser and more selective PEMs for the application of FO, NF, and (BW)RO using various approaches to control the PEM properties. Remembering the mentioned classical parameters to control the buildup of a PEM like salt concentration, pH, and PE type, in this thesis more parameters are explored in order to control the properties of the PEM. Post treatment steps and combining PEMs to control swelling, charge, and solute fluxes and adding aquaporin containing vesicles in order to control selectivity. Furthermore, this thesis explores the possibility of high performing PEM membranes for the application of nanofiltration and forward osmosis. Below I listed the chapters that are the backbone of this thesis with a concise explanation how the individual chapters fit in the broader picture.

Chapter 2: Annealing of polyelectrolyte multilayers for control over ion permeation

In this chapter, excessive extrinsic charge compensation (i.e. high salt concentration) is used to reverse the effect of excessive polycation overcompensation to create a stoichiometric charge balanced multilayer, and therefore, control over the ion permeation.

Chapter 3: Nafion-based low hydrated polyelectrolyte multilayer membranes for enhanced water purification

Here, a very hydrophobic polyelectrolyte – Nafion – is applied as a final layer (or post treatment step) to decrease the hydration of the multilayer in order to increase the density and selectivity of the multilayer.

Chapter 4: Asymmetric polyelectrolyte multilayer membranes with ultrathin separation layers for highly efficient micropollutant removal

This chapter uses two polyelectrolyte multilayers; one with a very high permeability and the other a with an exceptional high retention toward micropollutants. These two systems are combined to create a synergetic highly permeable and highly selective membrane.

Chapter 5: Role of polycation and crosslinking in polyelectrolyte multilayer membranes

In this chapter an unusual parameter is changed, namely the polycation within the multilayer. Here, a relation is drawn between the different multilayer structures and crosslinkability on the membrane performance.

Chapter 6: Polyelectrolyte multilayer membranes for the application of forward osmosis

PEM membranes are not the best separating barriers for high salt concentrated solutions like draw solutions in forward osmosis, however, 'leaky' membranes can obtain high pollutant retention. In this chapter, different multilayer structures and draw solutions are tested to study how PEM membranes can play a role in the forward osmosis application.

Chapter 7: Aquaporin containing polymersomes in polyelectrolyte multilayer membranes

This chapter explores the possibility of incorporating polymersomes that contain the natural aquaporin water channel for PEM membranes. The incorporation of the polymersomes into PEMs are studied and applied to the application of nanofiltration.

Chapter 8: Outlook

In this chapter there will be reflected on all the results obtained in this thesis and a future perspective will be shown how the field of PEM membranes can/needs to advance.

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Chapter 2

Annealing of Polyelectrolyte Multilayers for Control over Ion Permeation

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Abstract

Polyelectrolyte multilayer based membranes are highly promising systems to create stable and versatile nanofiltration membranes. One very popular and well-studied polyelectrolyte pair is the polycation poly(diallyldimethylammonium chloride) (PDADMAC) and polyanion poly(sodium 4-styrenesulfonate) (PSS), due to its excellent separation properties and high chemical and physical stability. Membrane charge can be easily controlled by simply terminating the multilayer by either PDADMAC or PSS. Unfortunately, a phenomenon that occurs during multilayer coating, is overcompensation by PDADMAC. In this study, we show that overcompensation of PDADMAC results in a positive surface charge even when the multilayer is PSS-terminated. In addition, we show that this leads to poorer membrane separation properties with sulfate retention decreasing from 94% to 39%. At the same time, we demonstrate that a so-called annealing cycle with a high salt concentration leads to recovery of the negative surface charge, increasing the sulfate retention from 39% to 95%. Even for multilayers at which no irreversible positive surface charge is measured, separation properties improved substantially (increasing sulfate retention from 94% to 97%, at a higher membrane permeability) after salt-annealing. We conclude, that post-treatment by salt-annealing results in an improved membrane performance and allows an additional degree of control over the membrane separation properties.

2.1 Introduction

In membrane filtration there are four types of membranes commonly used: microfiltration, ultrafiltration, nanofiltration, and (reverse or forward) osmosis membranes. [1] Micro- and ultrafiltration are pore-flow membranes and separation is based on their porous structures where reverse osmosis membranes (RO) are based on dense separating layers and separation takes place by means of solution-diffusion. [2] Nanofiltration (NF) membranes fall in the transition region between pore-flow and solution-diffusion membranes and typically have a dense separating layer which is more open than a RO membrane. [2] This dense separating layer – in both RO and NF membranes – is usually a thin film prepared by interfacial polymerization (IP). These membranes are termed thin film composite (TFC) membranes because of their selective top layer and porous support for mechanical strength, and are commercially widely available. [3] However, commercial RO and NF membranes are mostly based on a flat sheet configuration. To obtain a higher surface-to-volume ratio, hollow fiber membranes are of more interest. However, these are notoriously difficult to coat by IP. [4]

One recent breakthrough in membrane material science is an alternative to IP that allows coating of thin polymeric films (<50 nm) on a surface independent of its geometry. This versatile technique is termed layer-by-layer (LbL) assembly of polyelectrolytes, [5] in which two oppositely charged polyelectrolytes are coated alternately on a charged surface to create polyelectrolyte multilayers (PEMs). [6] The choice of polyelectrolyte pairs [7], salt concentration [8], and pH [9] are of great importance for the properties of the thin film. PEMs can be formed via several approaches including immersive, spin, spray, electromagnetic, and fluidic methods that each have their own advantages and disadvantages. [10] This breakthrough has led to an increasing interest in PEM-based membranes for both NF and RO applications. [11, 12] Various charged support surfaces such as poly(ethersulfone) [13], sulfonated poly(ethersulfone) [14], polysulfone [15], plasma treated poly(acrylonitrile)/poly(ethylene terephthalate) [16], and porous alumina supports [17] have been investigated. In most cases a tight ultrafiltration support membrane is used to quickly obtain a separation layer that has nanofiltration properties and a good coverage of the surface. Although several modified membranes have been studied based on various polyelectrolytes, special interest has been shown in PEM-membranes based on poly(diallyldimethylammonium chloride) (PDADMAC) and poly(sodium 4-styrenesulfonate) (PSS). This polyelectrolyte couple has been well studied for its anion selectivity towards fluoride [18], sulfate [19], and phosphate [20] and

outperforms most commercial membranes in terms of the combination of permeability and selectivity. Since most commercial nanofiltration membranes consist of a thin polyamide film, they are prone to degradation once the membrane is cleaned with hypochlorite. [14] PSS/PDADMAC membranes show superior chemical stability towards hypochlorite up to a hundred times higher in comparison with commercial polyamide-based membranes. [14]

In the formation of PEMs, increasing the salt concentration results in thicker PEMs at an equal number of layers. [21, 22] When a PEM is coated on top of a membrane, the pores of the membrane must first be closed until a defect-free separating layer can be formed. Two distinct regimes can be defined here: the pore-dominating regime and the layer-dominating regime. [23] When the salt concentration is increased, the layer-dominated regime is reached with fewer coating steps. From a manufacturing perspective it would be beneficial to coat PEMs at high salt concentrations in order to make the procedure less labor intensive. Unfortunately, a phenomenon that occurs when a PSS/PDADMAC multilayer becomes too thick is overcompensation of PDADMAC, thereby creating an excess of positive charge in the multilayer. [24] This phenomenon has been mainly observed at high salt concentrations, since thick layers are easily obtained at such high ionic strengths. [17, 22] In these studies, zeta potential measurements have shown that the multilayer becomes positive after a certain number of layers when coated at high ionic strengths. An excess of positive charge is expected to be undesirable for PEM-coated membranes for several reasons: excess charge will induce more swelling [25] and, in turn, lead to a more open and less selective layer. Moreover, positively charged layers tend to be more susceptible to fouling. [26]

A method to counteract the excess of positive charge was proposed by Fares et al. [27] who annealed PSS/PDADMAC multilayers with a 2 M NaCl salt solution. They showed that when PSS/PDADMAC multilayers are exposed to 2 M salt concentration, excess PDADMAC evenly disperses throughout the multilayer. This method is effective because PSS/PDADMAC multilayers undergo a glass transition for NaCl concentrations higher than 1.5 M or temperatures higher than 45°C. [28] Under these conditions, the excess of PDADMAC will reach the surface and for that reason will be able to take up PSS until the surface is saturated. Subsequently, multiple annealing cycles were performed to obtain a stoichiometric multilayer, which was reached after six annealing cycles.

In this work, for the first time, we show that salt-annealing of PSS/PDADMAC multilayers can be used to prepare PEM-coated membranes with excellent separation properties. We systematically study the buildup of positive charge in PSS/PDADMAC multilayer and the

negative impact this has on membrane performance. Moreover, we show that membrane performance can be recovered by annealing the PEM-based membranes. To do this, a PSS/PDADMAC multilayers are coated on hollow fiber membranes in a 1.0 M NaCl solution. The membrane performance is tested on the retention of mono- and divalent salts: NaCl, Na₂SO₄, and MgCl₂. To characterize the surface of the membrane, zeta potential and contact angle measurements are performed after each coated monolayer. These measurements allow us to understand why the membrane performance changes after each coating step and annealing cycle. Finally, we will show that the membrane becomes positively charged after a certain number of layers and that this affects the performance of the membrane. Through annealing, the charge can be reversed and we study the effect of the number of annealing cycles on the performance of the membrane.

2.2 Materials & Methods

2.2.1 Materials

Polyelectrolytes, poly(diallyldimethylammonium chloride) (PDADMAC, Mw=200,000-350,000 g·mol⁻¹, 20 wt.% in water) and poly(sodium 4-styrenesulfonate) (PSS, Mw=200,000 g·mol⁻¹, 30 wt.% in water) were purchased from Sigma-Aldrich. Sodium chloride (NaCl) was obtained from Akzo Nobel. Potassium chloride (KCl) was obtained from VWR. All chemicals were used without any further purification.

Hollow fiber membranes were obtained from NX Filtration B.V. (Enschede, the Netherlands) and are based on sulfonated poly(ether sulfone) (SPES) and PDADMAC. The fibers have a positive surface charge, a diameter of 0.68 mm, a standard permeability of 200 L·m⁻²·h⁻¹·bar⁻¹, and a molecular weight cut-off (MWCO) of 25 kDa. Silicon wafers were purchased from WaferNet Inc. (San Jose, USA).

2.2.2 Polyelectrolyte multilayer coating procedure

Hollow fiber membranes and silicon wafers underwent identical coating treatment, but they were coated separately. Hollow fiber membranes were coated in a bundle. Since the hollow fibers have a positive charge, silicon wafers were first dipped in a 0.1 g·l⁻¹ PDADMAC solution at a salt concentration of 1.0 M of NaCl. This was performed to make the comparison between hollow fibers and silicon wafers as equal, therefore, layer zero on silicon wafers is a PDADMAC layer. Subsequently, both hollow fibers and silicon wafers were dipped in a 0.1 g·l⁻¹ PSS solution at a salt concentration of 1.0 M of NaCl for at least

15 min. After coating the first polyelectrolyte layer, the membranes and wafers were rinsed three times for 5 min in separate rinsing baths containing 1.0 M of NaCl. After rinsing, the next layer was added by immersing the membranes and wafers in a 0.1 g·l⁻¹ PDADMAC solution at a salt concentration of 1.0 M of NaCl for at least 15 min. After this layer, the membranes and wafers were rinsed in the same fashion as the first layer. This procedure was repeated until the desired number of layers was obtained. Annealing was performed in cycles up to a maximum of six cycles, each cycle consists of three sequential steps. The first step is the immersion into a solution containing 2.0 M NaCl for 30 min, followed by the adsorption step in a 0.1 g·l⁻¹ PSS solution containing 1.0 M of NaCl for 5 min, and ended by a rinsing step with a solution containing 1.0 M of NaCl. After the coating and annealing procedures, the membranes were placed in an aqueous solution containing 15 wt.% glycerol for at least four hours and were subsequently dried overnight. Silicon wafers were blown dry by a stream of nitrogen and stored in a sealed petri dish before measuring.

2.2.3 Contact angle

Contact angles were measured using the captive bubble method. The captive bubble contact angle was measured on a Dataphysics OCA15 plus. To determine the contact angle a coated silicon wafer was placed coated-side-down in a cell filled with Milli-Q water. Subsequently a 5 µL air bubble was put on the surface of the silicon wafer. To calculate the contact angle a picture was taken five seconds after the air bubble touched the surface of the silicon wafer. Using the SCA20 software the contact angle was calculated. All measurements were performed in three-fold and the average values and the standard deviations were calculated and reported.

2.2.4 Ellipsometry

A rotating compensator ellipsometer (Mk-2000V, J.A. Woollam Co., Inc.) was used for the spectroscopic ellipsometry measurements and was operated in a wavelength range of 370–1000 nm. Samples were measured under three different angles of incidence (65, 70, and 75°) and at least three different spots on the silicon wafers were measured. All measurements were done under ambient conditions.

$$n(\lambda)=A+\frac{B}{\lambda^2} \quad (2.1)$$

Data fitting was performed using the CompleteEase software. A standard Cauchy model, shown in **Equation 2.1**, was used to fit the data of the polyelectrolyte multilayers. The refractive index of silica and its wavelength dependence is well known and defined. The

Cauchy parameters for the polyelectrolyte multilayers were independently fitted from the thickness for layers thicker than 30 nm. Average values with the standard deviations were calculated and reported.

2.2.5 Reflectometry

The growth of a polyelectrolyte multilayer was studied using reflectometry. This technique allows for a quantitative and in-situ measurement of the adsorbed amount when polyelectrolytes are coated alternately. [29] A silicon wafer is used in front of a flow cell and the adsorption is measured at the stagnation point. At this stagnation point, the hydrodynamics are well-defined and mass transfer is limited by diffusion. To build the PEM on top of the silicon wafer, polyelectrolyte solutions were alternately flown with rinsing steps in between. At every adsorption step, polyelectrolyte solution was flown long enough to create a stable adsorption value. Polyelectrolyte solutions containing $0.1 \text{ g}\cdot\text{l}^{-1}$ of polyelectrolyte and an ionic strength of 1.0 M NaCl were prepared. Adsorption took place under ambient conditions on a silicon wafer with a layer of 87 nm silicon oxide on top. During the entire experiment the ionic strength was kept constant to ensure a stable signal.

Reflectometry uses monochromatic light of a He-Ne laser (632.8 nm). The light is linearly polarized and is reflected from the wafer at the Brewster angle of 71° . Subsequently, the light is split into its parallel and perpendicular components in the detector. The ratio between the differences in these components relative to the initial state is proportional to the adsorbed amount of mass on the wafer as shown in **Equation 2.2**:

$$\Gamma = Q \cdot \frac{\Delta S}{S_0} \quad (2.2)$$

Where Γ is the adsorbed mass in $\text{mg}\cdot\text{m}^{-2}$ on the silicon wafer and S_0 is the initial signal of a bare silicon wafer at the start of the experiment. The sensitivity-factor, also known as the Q-factor, is dependent on the refractive indices (n), thickness of the adsorbed layers (d), angle of incidence (θ), and the refractive index increment (dn/dc) of the multilayers. An optical model was used to calculate the Q-factor of a multilayer made out of PDADMAC and PSS on a silicon wafer that had an 87 nm silicon oxide layer on top. The calculated Q-factor was $25 \text{ mg}\cdot\text{m}^{-2}$ for this case.

2.2.6 Zeta potential

To determine the zeta potential of the PEM-membrane, pre-coated hollow fiber membranes were placed in modules. Subsequently, the zeta potential was measured using an electrokinetic analyzer (SurPass, Anton Paar, Graz Austria). A 5 mM KCl solution was

pumped through the hollow fiber module under ambient conditions. The flow of the liquid under a given pressure difference through the hollow fiber module creates a streaming current. Knowing the measured streaming current (A), dI , and the applied pressure difference (Pa), dp , the zeta potential (V), ζ , can be calculated according to **Equation 2.3**:

$$\zeta = \frac{dI}{dp} \cdot \frac{\eta}{\epsilon \cdot \epsilon_0} \cdot \kappa_B \cdot R \quad (2.3)$$

Where η is the dynamic viscosity (Pa·s) of the electrolyte, ϵ the dielectric constant (-) of the electrolyte, ϵ_0 the permittivity of vacuum (F·m⁻¹), κ_B the specific electrical conductivity of the electrolyte solution (S·m⁻¹), and R is the ohmic resistance (Ω) of the cell measured. Every module was measured six times by the 5 mM KCl solution and for every measurement point three membranes were measured. From this data average values and standard errors were derived.

2.2.7 Membrane performance

To test the membrane performance, single hollow fibers were potted into modules with an effective membrane length of 17 cm. For every type of membrane, three single hollow fiber modules were made and tested in order to obtain average values and standard deviations. Salt retention measurements were performed using NaCl, Na₂SO₄, and MgCl₂ to measure the mono- and divalent salt rejection. The measurements were performed in crossflow mode at a transmembrane pressure of 2 bar and a crossflow velocity of 1 m·s⁻¹, which corresponds to a Reynolds number of 675 (laminar flow regime). To determine the retention, both the permeate and feed were measured using a WTW 3210 conductivity meter. Knowing the conductivity of the permeate and the feed, the retention can be calculated by dividing the difference of the conductivities by the feed conductivity, as follows:

$$R = \frac{\Delta C}{C_{\text{feed}}} \cdot 100\% \quad (2.4)$$

2.3 Results and Discussion

In this section, we will initially focus on the characterization of the PSS/PDADMAC multilayer prepared at an ionic strength of 1.0 M of NaCl by means of reflectometry, zeta potential, and contact angle measurements. Here, it is shown that the multilayer is successfully grown on porous hollow fiber supports and that the surface properties change as function of the multilayer thickness. In order to understand the change in surface properties, the PEMs are, in the second part, assessed for their ion rejection performance. We subsequently correlate the characterization results obtained in the first part to the ion rejection behavior obtained in the second part. This correlation provides an improved understanding of the ion rejection properties of the PSS/PDADMAC PEM as a function of the number of layers on the surface.

2.3.1 Polyelectrolyte multilayer characterization

Applying optical fixed angle reflectometry, the growth of PSS/PDADMAC multilayers at an ionic strength of 1.0 M NaCl on a silicon wafer was studied. Here, two polyelectrolyte solutions are alternately flown through the fluid cell where adsorption to a silicon wafer is measured. After each polyelectrolyte deposition, the cell was flushed with a solution containing the same ionic strength as the polyelectrolyte solution in order to prevent the formation of PDADMAC and PSS complexes. The point of measurement occurs at a stagnant point under well-defined hydrodynamic conditions on the silicon wafer. This means that at this point no shear is applied and adsorption only takes place based on diffusion. This is important since shear can influence the buildup of a polyelectrolyte multilayer. [30] When measuring at the stagnant point within the cell, the multilayer is formed via electrostatic interactions and a typical growth profile is obtained as shown in **Figure 2.1** with the adsorption on the left axis. This figure shows the non-linear-to-linear growth of PSS and PDADMAC under an ionic strength of 1.0 M of NaCl as was also shown by Dubas and Schlenoff [8], and McAloney et al. [21] The dry layer thickness on the right axis in **Figure 2.1** is calculated by dividing the adsorption data by the density of a PSS/PDADMAC multilayer of $1.07 \text{ g}\cdot\text{cm}^{-3}$. [31] In addition, dry layer thickness of the multilayer (shown in **Figure 2.1** by the red dots) was measured by ellipsometry; resulting in a thickness of a nine, thirteen, and seventeen thick layers being 32 ± 0.5 , 67 ± 2.8 , and $97\pm2.2 \text{ nm}$ respectively, further indicating a linear growth at thicker layers. The calculated and measured thicknesses are for dry layers, when these layers are immersed in water the thickness will increase due to swelling of the layers by 30 to 40%. [31]

Figure 2.1: multilayer growth measured using reflectometry and ellipsometry. On the left axis: adsorption ($\text{mg}\cdot\text{m}^{-2}$) of PSS (odd) and PDADMAC (even) at an ionic strength of 1.0 M NaCl on a silicon wafer is plotted as function of the number of layers to form a polyelectrolyte multilayer. On the right axis: dry layer thickness (nm) of the PSS/PDADMAC multilayer as function of the number of layers. The dry layer thickness is calculated by using a PSS/PDADMAC multilayer density of $1.07 \text{ g}\cdot\text{cm}^{-3}$ (black dots). Indicated by the arrow and red dots are the dry layer thicknesses of the PSS/PDADMAC multilayer measured by ellipsometry.

The PSS/PDADMAC multilayers were also coated on porous hollow fiber support membranes by dip-coating the supports alternately in the corresponding polyelectrolyte solutions. After each coating step the multilayer is rinsed with a solution containing the same ionic strength as the polyelectrolyte solutions. In dip-coating, adsorption of polyelectrolytes is based on diffusion just like in the reflectometry measurements. Therefore, the two coating procedures will lead to highly comparable PEM-coatings.

When coating the multilayer on a porous membrane support it is important to make sure that the multilayer covers all the pores. From literature it is known that a zig-zag behavior is observed in the permeability of the membrane when coating PSS and PDADMAC alternately. [22] This behavior is termed the odd-even effect and it occurs when two polyelectrolytes are alternatingly deposited on a surface. [32] This odd-even effect is also observed in membrane permeability measurements and is due to the difference in swelling of PDADMAC-terminated multilayers compared to PSS-terminated multilayers; where PDADMAC-terminated multilayers show a swelling that is much higher than for PSS-terminated multilayers.[33] When PEMs are coated on porous membrane supports, a

pore-dominated and a layer-dominated regime can be found. [22] In the pore dominated regime, a PDADMAC-terminated membrane shows a higher resistance than a PSS-terminated membrane, because the higher swelling of PDADMAC results in pore closure, an effective decrease in pore diameter. In the layer dominated regime, however, the higher swelling of PDADMAC gives a lower resistance, and therefore a higher permeability, because the entire multilayer becomes less dense. It is important to be in the layer dominated regime to ensure a defect free layer. In **Figure 2.2**, the permeability of the membrane is plotted as function of the number of layers. Here, it can be seen that the coated PEM-membrane has a permeability of around $4\text{--}10 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$, which is a typical value for NF membranes. A PSS-terminated multilayer has a lower permeability than a PDADMAC-terminated multilayer indicating the layer dominated regime. This means that the membrane is completely covered by the PEM and that the permeability and separation properties will be fully determined by the PEM.

Figure 2.2: permeability ($\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$) as function of the number of layers for a PSS/PDADMAC multilayer coated hollow fiber membrane prepared at 1.0 M of NaCl. The non-annealed multilayer is either terminated by PDADMAC, indicated by open squares, or PSS, indicated by black diamonds. Annealed PSS-terminated multilayers are indicated by red triangles.

To anneal the multilayer, the multilayer is immersed in a solution containing a high ionic strength of 2.0 M of NaCl which results in an increased mobility of the polyelectrolytes within the multilayer. [27] Afterwards, the membranes are dip-coated in the PSS polyelectrolyte solution at an ionic strength of 1.0 M of NaCl. The immersion and dip-

coating are considered as one annealing cycle; in total, six annealing cycles are applied to create an annealed multilayer. In a similar procedure described by Fares et al. [27] In that work, it was shown using radioactive labeled counter ions that with each annealing cycle more PSS is adsorbed. **Figure 2.2** shows that the permeability of the annealed membrane is higher compared to a non-annealed multilayer. This can be explained by the adsorption of more negative charges in the multilayer which leads to a higher degree of swelling, and supports the work of Fares et al. [27]

The zeta potential of the PEM-coated membranes was measured by means of streaming potential using hollow fiber membranes. Numerous studies have shown streaming potential measurements to be a viable method [34-37] and it is commonly used in a hollow fiber configuration. [14, 22, 38] Every layer of the membrane was prepared separately to give the most accurate result of the zeta potential, because the shear stresses accompanied with streaming potential measurements can influence the properties of the multilayer. [39] In this study, care was taken to produce every module in an identical fashion and various modules were measured in order to obtain a reliable result.

Figure 2.3: A: zeta potential of a PSS/PDADMAC PEM prepared at an ionic strength of 1.0 M NaCl as function of the number of layers. The PEM was coated on a hollow fiber support membrane. The solid line represents the normal PEM buildup, the dashed lines and the red triangles represents an annealed PEM. B: zeta potential as function of the number of annealing cycles for a PEM-coated hollow fiber membrane. The black solid line represents a multilayer of seventeen layers thick and the red solid line represents a multilayer of nine layers thick.

In **Figure 2.3A**, the typical zig-zag pattern is obtained that has been observed for many PEMs, [7, 17, 40] showing that the surface charge is positive after adsorption of the polycation and negative after polyanion adsorption. Already after the fourth layer, the zeta potential was positive when terminated with PDADMAC or neutral when terminated with PSS. This trend continues until the ninth layer. After the ninth layer, the zeta potential shifts to positive potentials. The potential of the multilayer stays positive even though the multilayer is terminated with the negatively charged PSS. This was also reported by Adusumilli et al. [17] and de Grooth et al. [22] for PEM-coated membranes prepared at ionic strengths of 1.0 M and 0.5 M of NaCl respectively. This is most likely due to the buildup of PDADMAC in the PEM bulk, as described by Ghostine et al. [24] and Fares et al. [27], Kelly et al. [41] In these works, an increasing amount of PDADMAC was observed throughout the multilayer for thicker multilayers. Arias et al. [42] showed even that excess PDADMAC, in a PSS-terminated multilayer, diffuses up to the surface over time when stored in saline water (0.15 M NaCl). In the present study, we show that a PSS/PDADMAC multilayer grown at an ionic strength of 1.0 M NaCl on a membrane surface, shows the same trend in the zeta potential measurements as the above mentioned studies. The measurements show that the surface properties are greatly influenced by the buildup of PDADMAC within the multilayer.

Annealing of the polyelectrolyte multilayer membranes was performed in six cycles using the procedure described earlier. In **Figure 2.3A**, as indicated by the dashed line, a nine and seventeen layer thick annealed multilayer had a negative zeta potential and not a positive zeta potential of a non-annealed PSS-terminated PEM. To investigate if the number of annealing cycles influenced the streaming potential, various membranes were measured for varying number of annealing cycles; as shown in **Figure 2.3B**. Here, it can be seen that for both a nine and seventeen layer thick PEM, the streaming potential reached its most negative value after the first annealing cycle. This means that the surface charge properties of the multilayer are not influenced by the number of annealing cycles, most likely due to the relatively thin multilayers used in this study in comparison to others [27] and the long annealing times used in this study. [43]

Figure 2.4: captive bubble contact angle of a silicon wafer coated with a PSS/PDADMAC multilayer as function of the number of layers. Odd layers are PSS-terminated multilayers and even layers are PDADMAC-terminated multilayers. Solid bars represent the non-annealed membranes and patterned bars represent the annealed membranes. The silicon wafers were immersed in water coated-side-down and an air bubble was released on the surface. The contact angle was extracted from the air/water interface.

The effect of annealing was also studied by contact angle measurements. Taking the captive bubble approach is essential here as it ensures that the multilayer is in its hydrated state and the contact angle measured is more accurate. From literature it is known that the contact angle of a multilayer is dependent on the terminating layer, creating a zig-zag pattern, and that a PDADMAC-terminated multilayer has a 10-40° higher contact angle than a PSS-terminated multilayer. [44-46] In **Figure 2.4**, the results of the contact angle measurements are presented and it is observed that a PDADMAC-terminated layer (eighth layer) has a 25° higher contact angle than a PSS-terminated layer (ninth layer). However, the difference between the contact angle of the twelfth and thirteenth layer is already smaller than 10°. Furthermore, no significant difference in the contact angle is observed between the sixteenth and seventeenth layer. This means that the zig-zag pattern disappeared and that the terminating layer is no longer influencing the multilayer properties. In addition, the contact angle of a PSS-terminated multilayer increases from 30° to 47°, comparing the ninth and the seventeenth thick layer, indicating a higher influence of PDADMAC. This result correlates well with the zeta potential results and is most likely due to the overcompensation of PDADMAC in the multilayer. Annealing of the multilayer shows, that the contact angle decreases to a value of around 30°, for the

thirteenth and seventeenth thick layer, indicating a higher influence of the surface from the PSS. This shows that annealing counteracts the overcompensation of PDADMAC as was also shown by the zeta potential results.

2.3.2 Salt retention of polyelectrolyte modified membranes

In the previous section, it was shown that the surface properties of thicker PSS/PDADMAC multilayers are dominated by PDADMAC, and that for thicker layers, the surface properties no longer depend on the terminating polyelectrolyte layer. It was also shown that annealing alters the surface properties of the multilayer and recovers the influence of PSS on the surface properties. In this section, we investigate how these changing surface properties influence the salt rejection of PEM-membranes and how the annealing cycles can help as a post-treatment step in regaining control over the membrane surface charge and thus the separation properties. For this study, three types of salts were investigated at a concentration of 5 mM: sodium chloride (NaCl), sodium sulfate (Na_2SO_4), and magnesium chloride (MgCl_2). Divalent salts were used, in addition to monovalent NaCl, because the PSS/PDADMAC multilayers are known for their high surface charge density and, therefore, the separation of ions is mainly based on Donnan exclusion. [22] To obtain insight into the effect of layer thickness, the membrane separation properties of a nine, thirteen, and seventeen layer thick PEM-membrane was studied. The results of the salt retention measurements are shown in **Figure 2.5**.

In **Figure 2.5A**, the retention of the negatively charged divalent sulfate ions across the membrane is plotted for various number of layers. A multilayer with an even number of layers is terminated with PDADMAC and a multilayer with an odd number of layers is terminated with PSS. Here, it can be observed that a multilayer with eight layers, PDADMAC-terminated, has a poor sulfate retention due to its positive surface charge. A multilayer with nine layers, PSS-terminated, has a much higher retention. When the multilayer becomes thicker, forming a thirteen and seventeen layer thick multilayer, the retention of sulfate ions drops tremendously due to the change in surface charge. This decrease in sulfate ion retention is in line with the observed increase in magnesium ion retention. Magnesium retention is high for PDADMAC-terminated layers and for thicker multilayers (both PDADMAC-terminated and PSS-terminated). In both cases, the multilayers have a positive surface charge which excludes the magnesium ions from the surface and the bulk of the film. For a thin multilayer ended on PSS, magnesium retention is lower due to the almost neutrally charged surface (see **Figure 2.5B**).

Figure 2.5: sodium sulfate (Na_2SO_4) (A), magnesium chloride (MgCl_2) (B), sodium chloride (NaCl) (C) retention of PSS/PDADMAC multilayer coated hollow fiber membranes prepared at an ionic strength of 1.0 M of NaCl for various number of layers. The solid bars correspond to the retention of the normal PEM-coated membrane. The patterned bars are the retention values for the annealed PEM-membranes. All membranes underwent six annealing cycles. D: sodium sulfate retention as function of the number of annealing cycles.

The effect of annealing on the membrane performance is shown by the dashed columns in **Figure 2.5**. Since the PDADMAC/PSS multilayer separates ions on the basis of Donnan exclusion, the effect of annealing (shown in **Figure 2.5A, B, and C** by the dashed columns) on the sulfate retention (**Figure 2.5A**) is high for those membranes with thirteen and seventeen layers. The retention of sulfate ions increased from 38% to 95%

after annealing. The sulfate retention of the multilayer with nine layers also substantially improved (94% to 97%, thereby halving sodium sulfate permeation), in agreement with the observed more negative zeta potential (**Figure 2.3B**) instead of a neutral zeta potential. These results are also in agreement with the ferricyanide permeability through PSS/PDADMAC multilayers, before and after annealing, in the study of Kelly et al. [41] Since the zeta potential is negative after annealing, the retention of magnesium (shown in **Figure 2.5B**) drops greatly for all PSS-terminated multilayers that vary by thickness. For sodium chloride (shown in **Figure 2.5C**), the retention for non-annealed membranes is higher when the multilayer is terminated on PDADMAC. This can be explained by the higher surface charge as also shown by the zeta potential measurements, resulting in a stronger exclusion of sodium ions. Interestingly, for the thinnest layer studied (nine layer thick multilayer), the retention increased when the multilayer is annealed. This is in contrast to the other thicknesses where no significant differences were measured. This is expected to be due to the neutral multilayer becoming negatively charged; in this way, the chloride ions are excluded more strongly.

Surprisingly, in **Figure 2.5B** a slight increase in the magnesium retention as function of the layer thickness is observed for annealed multilayers. It suggests that the PEM is getting denser, since the sulfate retention does not change as function of the thickness. However, no increase in the sodium chloride retention and no decrease in the permeability is observed. This could be, as described earlier, due to the annealing procedure. The annealing procedure is the same for every PEM-membrane. However, when the multilayer is thicker, more PDADMAC is present in the bulk of the multilayer and more annealing cycles are needed to complex all the excess PDADMAC with PSS. [27] Although, in comparison to the previous study, relative thin layers are used in this study. It could be that a thicker multilayer contains more positive charges inside than a thinner layer and that annealing is less successful for thicker multilayers.

All membranes were annealed six times in total. As for the zeta potential measurements, membrane performance was also assessed as function of the number of annealing cycles. In **Figure 2.5D**, the sulfate retention is plotted as a function of the number of annealing cycles. Here, the retention does not depend significantly on the number of annealing cycles. This relates to the results obtained from the streaming potential measurements, where the surface charge after the first annealing cycle was the same as after the last annealing cycle. Clearly, one single annealing cycle is sufficient to regain the expected high sulfate retentions.

2.4 Conclusions

This is the first study to show that polyelectrolyte multilayer (PEM) post-treatment by salt-annealing can be used to gain control over the surface charge of PEM-membranes. In this study, we show that the surface properties of PSS/PDADMAC multilayer membranes become dependent on the properties of PDADMAC. For this reason, the surface properties do not depend anymore on the terminating layer, due to the overcompensation of PDADMAC at thicker layers. The surface charge increases irreversibly to positive values and also contact angles show a high influence of PDADMAC at thicker layers. It is shown that the change in surface properties has a tremendous effect on the separation properties of the PEM-membrane. Sulfate retentions drop from 94% to 39% and magnesium retentions increase from 59% to 87% for PSS-terminated layers, showing that control of the membrane separation properties is lost. Annealing of PSS/PDADMAC multilayers was shown to be effective in order to counteract the overcompensation of PDADMAC and regain control over the membrane separation properties. We show that just a single salt-annealing cycle is enough to regain control over the surface charge of the membrane. For thicker multilayers at which PDADMAC starts to dominate, sulfate retention was increased from 39% to 95% at higher or equal permeability. Even for a multilayer with nine layers, at which PDADMAC is not dominating, salt-annealing can halve sulfate permeation (sulfate retention increased from 94% to 97%) in combination with a higher permeability. Clearly, applying salt-annealing as a post-treatment step allows an important additional degree of control over ion permeation. Moreover, the work presented here opens the door to use more annealing approaches to further optimize PEM-membrane performance.

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Chapter 3

Nafion-based Low Hydrated Polyelectrolyte Multilayers for Enhanced Water Purification

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Abstract

The increase of micropollutant concentration in both surface and ground water is an emerging concern for the environment and human health. Most of such small organic molecules (medicines, hormones, and plasticizers) enter the environment via our wastewater, because they are not sufficiently removed by the current techniques applied in wastewater treatment plants. A possible solution to remove micropollutants is the usage of polyelectrolyte multilayer (PEM) based membranes. PEM membranes have received a growing interest in the last decade due to their high chemical and physical stability, and their high permeability and selectivity. A popular polyelectrolyte pair to make dense PEM membranes with high salt retentions is the combination of poly(allylamine hydrochloride) (PAH) and poly(sodium 4-styrene sulfonate) (PSS). Unfortunately, smaller micropollutants (such as bisphenol A, sulfamethoxazole, Naproxen, and bezafibrate) still show significant permeation through this membrane. In this study, for the first time, a single final layer of Nafion is applied on the PEM to increase the density of the PEM membrane. It is shown that when terminating with Nafion, the swelling of the multilayer decreases by 50%. These pronounced changes in layer structure are reflected by changes in membrane performance, such as a lower molecular weight cut-off (MWCO) and an increasing hydraulic membrane resistance. Furthermore, we show that the Nafion content of the multilayer can be increased by constructing a Nafion/PAH multilayer on top of the existing PSS/PAH multilayer thereby lowering the molecular weight cut-off. Although hydraulic resistance increases, these novel PSS/PAH/Nafion based multilayers show excellent performance in rejecting difficult-to-remove micropollutants, that have low molecular weight (200 to 650 Dalton) and different charges. Overall, a cocktail of 8 small micropollutants can be removed up to 97% by these membranes, allowing strongly enhanced water purification.

3.1 Introduction

Growing concentrations of micropollutants in our surface and our drinking water sources lead to increased worries about their long and short term effects on human health and environment. [1] Wastewater from hospitals, industry, and domestic households contains a large variation of small (100-1000 Dalton) and difficult-to-remove micropollutants (MPs). Unfortunately, traditional wastewater treatment based on flotation, clarification, and (an)aerobic treatment only removes a small amount of these micropollutants from waste streams. [2] The purified water, still containing MPs, is discharged in rivers and other drinking water resources. [3, 4] To prevent any micropollutants from ending up in our drinking water, membrane filtration of ground and surface water can be a solution to provide clean and safe drinking water. Alternatively, membranes could be used in wastewater treatment to prevent micropollutants from being released into the environment at all. For both possible treatment options, it is clear that better membranes need to be developed in order to remove micropollutants in an effective and efficient way.

In membrane science, various types of filtration exist, namely: microfiltration, ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). Where microfiltration and ultrafiltration are based on pore-flow membranes, reverse osmosis membranes have a dense separation layer, and therefore, the solution-diffusion principle applies. [5] NF membranes have properties in between RO and UF, but typically share the dense polymeric top layer of RO. NF has been found to separate on principles of Donnan, dielectric, and size exclusion. [6, 7] Nowadays, most NF membranes are thin film composite membranes consisting of a porous support, coated with a dense polyamide separation layer prepared by means of interfacial polymerization (IP). [8] While these membranes are very successfully applied for, e.g., hardness removal, their preparation technique has limitations. For example, it is very difficult to utilize IP coating for the inside of a hollow fiber membrane, while this geometry would hold many benefits in wastewater treatment, such as a high packing density and lower fouling potential. Moreover, IP based coatings are chemically weak and prone to degrade when treated with chemical cleaning agents. [9]

An upcoming technique to prepare NF membranes is Layer-by-Layer (LbL) assembly of oppositely charged polyelectrolytes. This highly effective method makes use of alternating deposition of two oppositely charged polyelectrolytes on a support membrane, independent of the support membrane geometry. This allows efficient fabrication of hollow fiber NF membranes, with the separating layer on the inside of the hollow fiber

membrane. Furthermore, the LbL technique allows easy finetuning of the resulting membrane properties, by control over the used polyelectrolytes [10] and the coating conditions, such as salt concentration [11] and pH [12]. Fabrication of PEM based hollow fiber membranes can be performed using simple immersive techniques like dip-coating [11] or by dynamically coating [13] polyelectrolytes on the surface by flushing the membrane with appropriate polyelectrolyte solutions. To coat a PEM, various charged support-surfaces can be used, including sulfonated poly(ether sulfone) [9] and plasma treated poly(acrylonitrile) [14]. It has been shown that a higher charge density of the support layer creates more stable PEM membranes. [9]

One commonly used polyelectrolyte pair to manufacture NF membranes is the combination of poly(styrene sulfonate) (PSS) and poly(diallyl dimethylammonium chloride) (PDADMAC). [15] This system has many advantages such as; good permeability, high multivalent ion retention, and a very high physical and chemical stability. However, major drawbacks of PSS/PDADMAC based PEM membranes are the relatively high molecular weight cut-off (MWCO) and thus low rejections of micropollutants. [11, 15] To obtain better retention performance towards MPs, membranes need to be designed with much more effective size-based exclusion, and thus a lower MWCO. A polyelectrolyte couple that has a denser structure, a high retention towards solutes, and still a high chemical and physical stability is the combination of PSS and poly(allylamine hydrochloric acid) (PAH). This polyelectrolyte couple leads to PEMs with a bulk excess of positive charge, resulting in a high retention towards ions. [16, 17] Furthermore, PSS/PAH based membranes have a small effective pore size (estimated to be 0.34 to 0.5 nm, depending on the pH of PAH during coating), which results in a high retention towards uncharged solutes. [18, 19] Still, we believe that it is required to densify this layer even further, to attain the required selectivity to remove small and uncharged MPs such as bisphenol A sufficiently.

Nafion is a well-known material used for the fabrication of high-performance ion exchange membranes (IEMs) for electrodialysis/electrolysis and fuel cell applications. [20, 21] Indeed, Nafion based membranes are amongst the densest ion exchange membranes in production, caused by the hydrophobic nature of the fluorinated polymer, leading to very high ionic selectivities. Even so, the selectivity between monovalent and divalent ions can still be increased by simply coating the surface of IEMs [22] and more specifically Nafion based IEMs [23] with PEM based coatings. In this study, however, we propose to reverse this approach by utilizing Nafion to achieve denser and more selective PEM based membranes. It has been shown, on model surfaces, that in combination with PDADMAC

or PAH a PEM can be constructed with Nafion acting as the polyanion. [24-27] Constructed PEMs with Nafion have been shown to be very hydrophobic even when a 'normal' PEM is terminated by just a single layer of Nafion, a so-called Janus film. [28]

In this work, we demonstrate for the first time that a Nafion coating can be applied as a post-treatment to create low-hydrated PEM membranes with an increased micropollutant retention. We study how Nafion impacts the swelling and hydrophilicity of a PSS/PAH multilayer and the effects on membrane performance. To characterize the multilayer, ellipsometry is used to study the swelling of the multilayer before and after terminating with Nafion. In addition, contact angle measurements are performed to study the hydrophilicity. Membrane performance is studied by measuring the hydraulic resistance after each coating step of PSS, PAH, and Nafion. Finally, we will show that through terminating with Nafion, the multilayer has a lower MWCO, a higher retention for micropollutants, but will keep the same salt retention behavior.

3.2 Materials and Methods

3.2.1 Materials

Poly(allylamine hydrochloric acid) (PAH, $M_w=150,000 \text{ g}\cdot\text{mol}^{-1}$, 40 wt.% in water) was purchased from Nittobo Medical, Japan, while poly(sodium 4-styrenesulfonate) (PSS $M_w=200,000 \text{ g}\cdot\text{mol}^{-1}$, 30 wt.% in water) and Nafion (1100 E.W. (Equivalent Weight) perfluorinated resin solution, 5 wt.% in lower aliphatic alcohols and 15-20% water) were purchased from Sigma-Aldrich. Sodium chloride was obtained from Akzo Nobel, The Netherlands, and sulfamethoxazole from Fluka. All other chemicals were obtained from Sigma Aldrich. All chemicals were used without further purification.

Tight hollow fiber ultrafiltration membranes were obtained from NX Filtration B.V. (Enschede, the Netherlands). The membranes are asymmetric with the smallest pore size at the inner surface. The fibers have a positive surface charge, an inner diameter of 0.68 mm, a standard permeability of $200 \text{ l}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$, and a molecular weight cut-off (MWCO) of 25 kDa. Silicon wafers were purchased from WaferNet Inc. (San Jose, USA).

3.2.2 Dip coating

Silicon wafers were first immersed, for 15 minutes, in a solution of $0.1 \text{ g}\cdot\text{l}^{-1}$ PAH and 0.5 M NaCl at a pH of 1.8. Subsequently, they were rinsed three times for 5 minutes in separate baths containing 0.5 M NaCl. After the rinsing steps, the wafers were immersed in a solution of $0.1 \text{ g}\cdot\text{l}^{-1}$ PSS and 0.5 M NaCl. After the second dip-coating step, the silicon wafers were rinsed in the same manner as the first dip-coating step. This cycle completes one [PAH/PSS] bilayer and is repeated with the same solutions until the desired number of [PAH/PSS] bilayers is reached. For hollow fiber membranes the dip-coating procedure is similar, with all coating and rinsing solutions always containing the same concentration of NaCl (50, 100, 500, or 1000 mM). However, for the hollow fiber membranes, the first step is to immerse them in the PSS solution instead of the PAH solution. Hollow fibers are completely immersed in an upright position in the coating and rinsing solutions to make sure that all air escapes from the inside of the fibers, such that the coating as well as the rinsing solutions are in contact with the entire inner surface of the fibers.

Nafion was coated on top of a $[\text{PSS}/\text{PAH}]_n$ multilayer (PAH $[\text{PSS}/\text{PAH}]_7$ for silicon wafers) by dipping the hollow fiber membranes or silicon wafers in a solution of 80/20 wt.% ethanol/water containing $0.1 \text{ g}\cdot\text{l}^{-1}$ of Nafion. The wafers and hollow fibers were first rinsed by a solution of 80/20 wt.% ethanol/water and subsequently by demineralized water before storage in demineralized water.

When building a [Nafion/PAH] multilayer, the demineralized water rinsing step is substituted by two rinsing steps containing the same ionic strength as the PAH coating solution. After rinsing, the fibers are immersed in a solution of 0.1 g·l⁻¹ PAH, at a pH of 1.8, and at the appropriate ionic strength. After PAH coating, the fibers were rinsed twice with the same ionic strength as the coating solution and one time in demineralized water, no pH adjustment to these rinsing solutions was performed. This cycle completes one [Nafion/PAH] bilayer, the cycle is repeated until the desired number of bilayers is obtained.

After dip coating is completed, the hollow fiber membranes are immersed in an aqueous solution containing 15 wt.% of glycerol for at least 4 hours. Subsequently, the hollow fiber membranes are dried overnight and potted into single hollow fiber modules with an approximate active fiber length of 17 cm.

3.2.3 Ellipsometry

A rotating compensator ellipsometer (Mk-2000V, J.A. Woollam Co., Inc.) was used for the spectroscopic ellipsometry measurements. The ellipsometer operates in a wavelength range of 370–1000 nm. Firstly, wet thicknesses were measured for the as prepared wafers that were stored for at least 24 hours in demineralized water. Wet thicknesses were measured by a 5 ml heated liquid cell filled with Milli-Q water at a 75° angle of incidence under ambient temperature. The coated wafers were equilibrated for 30 minutes in the liquid cell before measuring. After measuring the wet thickness, the wafers were dried using a nitrogen gas flow. Dry thicknesses were measured under three different angles of incidence (65°, 70°, and 75°) and at three different spots on the silicon wafers. All dry thickness measurements were done under ambient conditions.

$$n(\lambda) = A + \frac{B}{\lambda^2} \quad (3.1)$$

Data fitting was performed using the CompleteEase software. A Cauchy model, shown in **Equation 3.1**, was used to fit the data obtained from the coated silicon wafers. The refractive index of silica and its wavelength dependence is well known and defined. For the polyelectrolyte multilayers, the Cauchy parameters were fitted independently from the thickness for layers thicker than 30 nm. The swelling ratio for the multilayers was calculated using the dry and wet thickness, as shown by **Equation 3.2**. Average values and standard deviations of the thicknesses and swelling ratios were calculated and reported.

$$SR = \frac{d_{\text{wet}} - d_{\text{dry}}}{d_{\text{dry}}} \cdot 100\% \quad (3.2)$$

3.2.4 Contact angle

Contact angles were measured statically on a Dataphysics OCA15 plus and calculated by using the SCA20 software. To determine the contact angle, a coated silicon wafer was placed on a flat surface. Subsequently, a 5 μl water droplet (Milli-Q, 18.2 M Ω) was placed on the surface of the coated silicon wafer. To obtain the contact angle, a picture was taken five seconds after the water droplet touched the surface. All measurements were performed at least three times and the average values and standard deviations were calculated and reported.

3.2.5 Membrane resistance

The hydraulic resistance of the membranes towards water is determined by measuring the permeability of the polyelectrolyte multilayer membranes. At least three single hollow fiber modules were made for every membrane type and tested using a crossflow setup operated by a rotary vane pump (BN71B4 pump motor, Bonfiglioli, Italy; IMTI 1.5M inverter, Electroil, Italy; PA411 pump head, Fluid-o-Tech, Italy). Permeability was measured at 7.9 bars of applied pressure under crossflow conditions and the resistance of the membranes was calculated using **Equation 3.3** below. In this equation, ΔP is the transmembrane pressure (Pa), μ the dynamic viscosity (Pa·s), and J is the membrane flux ($\text{m}\cdot\text{s}^{-1}$).

$$R = \frac{\Delta P}{\mu \cdot J} \quad (3.3)$$

3.2.6 Molecular weight cut-off

Molecular weight cut-off was determined with a feed mixture of several poly(ethylene glycol) (PEG) molecules of different molecular weights; PEG200, PEG400, PEG600, PEG1000, and PEG1500 at a concentration of 1 g·l⁻¹ each. The crossflow setup was operated at 1.7 bar and a flow of 10 l·h⁻¹ per module. Feed and permeate samples were analyzed via Gel Permeation Chromatography with a size exclusion column (SEC) (Agilent 1200/1260 Infinity GPC/SEC series, Polymer Standards Service data center and column compartment). Solutions were flown at 1 ml·min⁻¹ over two Polymer Standards Service Suprema 8x300 mm columns in series: 1000 Å, 10 μm followed by 30 Å, 10 μm . Concentrations were measured via refractive index measurements.

3.2.7 Salt retention

Salt retention was measured in crossflow mode using 5 mM of NaCl, Na₂SO₄, MgCl₂, or MgSO₄. The measurements were performed in the laminar flow regime at a crossflow velocity of 1 m·s⁻¹ (equal to a Reynolds number of 675) using a transmembrane pressure of 1.7 bar. To determine retention, the conductivity of both the permeate and feed was measured using a WTV 3210 conductivity meter. Using **Equation 3.4**, the retention can be calculated based on the difference in conductivity of the feed and permeate.

$$R = \frac{\Delta C}{C_{\text{feed}}} \cdot 100\% \quad (3.4)$$

3.2.8 Micropollutant retention

To measure micropollutant retentions, a cocktail was prepared containing 3 mg·l⁻¹ of each of the micropollutants (atenolol, atrazine, bezafibrate, bisphenol A, bromothymol blue, naproxen, phenolphthalein, and sulfamethoxazole) and adjusted to a pH of 5.8. The measurements were performed at equal flux, therefore, the crossflow setup was operated at 1.2, 2.0, and 7.9 bar and at a crossflow velocity of 1 m·s⁻¹ per module. The separation process was allowed to stabilize for at least 24 hours per measurement while leading permeate back into the feed, to prevent that adsorption leads to a higher apparent retention. Subsequently, around 2 ml of permeate was collected from each module and a calibration range was prepared from the feed. All samples were analyzed by HPLC (High pressure liquid chromatography, Dionex Ultimate 3000, eluent: water, acetonitrile, and 0.1% phosphoric acid) over a Thermo Scientific Acclaim RSLC 120 C18 column (2.2 µm, 2.1x100 mm). Micropollutant concentrations were determined via UV/Vis detection at 225 nm, bromothymol blue at 430 nm. Subsequently, retention was calculated in the same way as salt retention, using **Equation 3.4**.

3.3 Results and Discussion

The results and discussion section is split into three distinct parts. In the first section, we focus on the characterization of PSS/PAH and PSS/PAH/Nafion multilayers prepared on model surfaces (silicon wafers with a 1.8 nm top layer of silica). We utilize static contact angle and ellipsometry measurements to obtain a measure for the hydrophilicity, thickness, and swelling of the multilayer. Here, it is shown that the swelling and hydrophilic properties of the multilayer change when terminated with Nafion. In the second part, the same multilayer is built on porous hollow fiber support membranes and characterized by membrane permeability measurements in order to understand the effect of Nafion on the hydraulic resistance of the PEM membrane. In the third part, the modified membranes are assessed on their performance by salt retention, molecular weight cut-off (MWCO), and micropollutant retention measurements. By correlating the results of the model surface characterization with membrane performance, a much better understanding is achieved on how Nafion affects the properties and performance of PEM membranes.

3.3.1 Polyelectrolyte multilayer characterization – Model surface

The effect of the terminating layer on a PSS/PAH multilayer was studied by contact angle measurements. From literature it is known that the contact angle of a PSS/PAH multilayer is around 30° to 60° [29] and depends on the terminating layer. When PSS and PAH are alternately coated on a silicon wafer, a zig-zag pattern is observed in the contact angle. It is known that the contact angle of a PAH terminated multilayer is 10° to 25° higher than when the multilayer is terminated with PSS. In this study, a PSS/PAH multilayer with 4.5 and 5.0 bilayers, and 7.5 and 8.0 bilayers terminated either on PAH or PSS, respectively, give the expected contact angle of around 30° to 60°, as shown in **Table 3.1**. Nafion deposited as the final layer instead of PSS increases the contact angle of the total multilayer to around 95°. This obtained contact angle is in agreement with literature values of Nafion thin films, these films have a contact angle of 95° to 106° [30, 31]. In addition, Ghossoub et al. [28] fabricated Nafion terminated PSS/PDADMAC multilayers to make Janus nanofilms which have a hydrophobic and a hydrophilic side. The contact angles measured in their work of around 95° is in agreement with contact angles obtained in this study. The results discussed here, clearly demonstrate that just a single layer of Nafion can significantly affect the PEM properties.

Table 3.1: Contact angles of [PAH/PSS]₄PAH and [PAH/PSS]₇PAH multilayers terminated by PAH, PSS, or Nafion. Both PAH and PSS were coated at 500 mM of NaCl and the former at a pH of 1.8. Nafion was coated in a mixture of 80/20 wt.% of ethanol/water. Error bars: standard deviation; n≥3.

	Contact angle (°)		Contact angle (°)
[PAH/PSS] ₄ PAH	43 ± 1	[PAH/PSS] ₇ PAH	54 ± 2
[PAH/PSS] ₅	38 ± 1	[PAH/PSS] ₈	36 ± 1
[PAH/PSS] ₄ Nafion	94 ± 3	[PAH/PSS] ₈ Nafion	92 ± 2

The same silicon wafers were studied by ellipsometry to determine the thickness both in dry and wet conditions. The dry-thicknesses of the individual multilayers are 20±1, 23±0.5, and 23±1 nm for the 4.5 and 5.0 bilayer thick multilayer and 30±0.6, 32±0.4, and 33±0.3 nm for the 7.5 and 8.0 bilayer thick multilayer, terminated on PAH, PSS, and Nafion respectively. From both the dry- and wet-thicknesses, the swelling ratio can be calculated according to equation 2, this result is plotted in **Figure 3.1**. Here, it can be observed that the swelling of the 5.0 bilayer thick multilayer is always higher than the 8.0 bilayer thick multilayer with the same final layer. This observation is in agreement with literature where it is shown that a PSS/PAH multilayer is more hydrated at smaller layer numbers and that the swelling reaches a stable value of around 20% at higher layer numbers. [29] Furthermore, it can be seen that the swelling degree changes significantly when the PSS/PAH multilayer is terminated by a single layer of Nafion, with swelling degrees decreasing by half to 10% to 15%. A Nafion terminated multilayer is thus much less hydrated than a normal PSS/PAH multilayer. For PEM based membranes, it is well established that the hydration of the layer is seen as a good indication of its separation performance, with a denser layer leading to higher hydraulic resistances for water permeation, but also to higher retention. [11, 32]

Figure 3.1: Swelling degree of a [PAH/PSS]₄PAH and [PAH/PSS]₇PAH multilayer terminated by PAH, PSS, or Nafion. By measuring the dry- and wet-thicknesses of the multilayers, equation 2 is used to calculate the swelling. Both PAH and PSS were coated with an ionic strength of 500 mM of NaCl and PAH at a pH of 1.8. Nafion was coated in a mixture of 80/20 wt.% of ethanol/water. Error bars: standard deviation; $n \geq 3$.

3.3.2 Polyelectrolyte multilayer characterization – Hollow fiber membrane

In this part, the PSS/PAH multilayers were coated on porous hollow fiber supports by alternately dipping the supports in the corresponding polyelectrolyte solutions in the same manner as the silicon wafers. After a polyelectrolyte coating step, the hollow fiber membranes were rinsed in rinsing solutions with the same ionic strength as the polyelectrolyte dipping solutions. This procedure leads to similar coatings both on asymmetric hollow fibers supports as on the silicon wafers. [11] When a PEM is coated on the support by means of dip-coating, the inner as well as the outer support surface will be coated. However, a separation layer is formed only on the inside, because of the smaller pores that can be completely closed by the PEM. It is important to obtain 100% pore closure in order to have a defect-free separation layer. When two different polyelectrolytes are adsorbed alternately on the surface, a zig-zag pattern in the permeability as function of the number of layers is typically observed. [11] This zig-zag pattern stems from the so-called odd-even effect and results from the difference in multilayer swelling depending on the final layer. [33] In the PEM membrane literature, the odd-even effect is used to distinguish the pore- and layer-dominated regime. [11, 15, 34] During the initial coating steps, the PEM is coated on the inside of the pores and narrowing them, but the pores still

define the separation properties until in the layer-dominated regime, at which the pores are completely closed by the PEM. In the pore-dominated regime, the polyelectrolyte with the largest multilayer swelling has the highest hydraulic resistance against water permeation, as layer swelling directly leads to narrower pores. On the contrary, in the layer-dominated regime the polyelectrolyte with the largest swelling has a lower hydraulic membrane resistance, as water can more easily permeate the more swollen layer. [11] Therefore, changes in hydraulic resistance can provide important information on the structure of the PEM membrane.

In **Figure 3.2A** and **B**, the hydraulic membrane resistance of a $[\text{PSS}/\text{PAH}]_n$ multilayer (black line) and a $[\text{PSS}/\text{PAH}]_n$ Nafion multilayer (red line) fabricated at 100 mM and 1000 mM NaCl is plotted against the number of bilayers. For both systems, a thicker multilayer leads to a higher hydraulic resistance, with an especially strong increase between 1 and 3 bilayers, indicative of the pores being closed by the PEM. For the PSS/PAH based multilayer no strong zig-zag effect is observed, in line with the small changes in hydration between PSS and PAH terminated layers (**Figure 3.1**). However, termination with Nafion leads to significantly different hydraulic membrane resistances, most likely due to the much lower hydration of the layer. Initially, for a multilayer of 1.5 bilayers thick, the hydraulic membrane resistance for Nafion terminated PEMs is lower than for the equally thick PSS terminated layers, in line with the effects expected for a pore-dominated regime where less swelling leads to a more open pore. For thicker layers (from 3.5 bilayers onwards) we observe the opposite effect, the less hydrated Nafion terminated multilayers have a higher hydraulic membrane resistance than the PSS terminated layers. This is exactly what is expected in the layer-dominated regime, at which all water needs to permeate through the PEM and at which a less swollen PEM leads to a higher hydraulic resistance. At 2.5 bilayers, the hydraulic resistance for a Nafion and PSS terminated multilayer is similar, which indicates a transition region between the pore- and layer dominated regime. Here, the low hydration of Nafion terminated PEMs provides very useful information on the structure of the prepared PEM membranes. It is observed that Nafion terminated multilayers lead directly to higher hydraulic membrane resistances, which could also be an indication for better selectivities. If we compare the data from the multilayers built at 100 mM and 1000 mM of salt, the trends are similar. However, the increase in hydraulic resistance from Nafion termination seems to be higher at high salt concentrations, especially for thicker layers. This effect of ionic strength was subsequently studied in more detail.

Figure 3.2: Hydraulic membrane resistance as function of the number of bilayers for a PSS/PAH multilayer built at a salt concentration of 100 mM (A) and 1000 mM (B) of NaCl. The black line represents the $[\text{PSS}/\text{PAH}]_n$ multilayer at which PSS terminated multilayers are half numbers and PAH terminated multilayers are full numbers. The red line represents a $[\text{PSS}/\text{PAH}]_n\text{Nafion}$ multilayer that is terminated with one Nafion layer on top of a PAH layer. Error bars: standard deviation; $n \geq 3$.

In **Figure 3.3**, the hydraulic membrane resistance of PSS/PAH multilayers built at various salt concentrations (50, 100, and 500 mM) is shown for layer thicknesses well in the layer-dominated regime of 6.5, 7, and 7.5 bilayers thick. It can be observed at all salt concentrations, when terminating on PAH, that the hydraulic resistance increases since the multilayer thickness increases. Furthermore, the hydraulic resistance of the membrane increases when the multilayer is coated at higher salt concentrations. This increase in hydraulic resistance is due to the higher ionic strength, at which thicker PEMs are formed. When this multilayer is terminated by Nafion (grey bars), the increase in hydraulic resistance is much higher than at low ionic strength. This could be due to the increased mobility of polyelectrolyte chains, [35] as Nafion chains could mix with the PSS/PAH layers below, which could lead to higher adsorption and a much stronger effect of Nafion as a final layer. At lower ionic strengths, a smaller effect on hydraulic resistance is observed, because less Nafion would be adsorbed due to the lowered mobility.

Figure 3.3: Multilayer in the layer-dominated regime at various salt concentrations. In both graphs the hydraulic resistance of the membrane as function of the building salt concentration is plotted. Black bars represent a PSS terminated multilayer, patterned bars a PAH terminated multilayer, and grey bars a Nafion terminated multilayer. Error bars: standard deviation; $n \geq 3$.

3.3.3 Membrane performance

In the previous sections, polyelectrolyte multilayer (PEM) characterization was discussed, both on model surfaces and hollow fibers. We clearly demonstrated that by terminating a PSS/PAH multilayer with Nafion, the swelling decreases, resulting in an increased hydraulic membrane resistance. In this section, we study how these changes in layer structure affect the membrane separation properties by means of salt retention, molecular weight cut-off (MWCO), and micropollutant retention. We focus here on membranes prepared at high ionic strength, as in these conditions the change in hydraulic resistance was the most significant. Moreover, we compare layers terminated by either PSS or Nafion. Negatively charged membranes are highly favored for water treatment[36] and the comparison is more fair as the membrane surface charge can already significantly affect the retention of charged species. The retentions of various types of salts (NaCl , Na_2SO_4 , MgCl_2 , and MgSO_4) are measured to obtain a good understanding of the multilayer separation properties towards differently charged ions. Finally, we evaluate if the membranes could be made even denser by building a $[\text{Nafion}/\text{PAH}]_6\text{Nafion}$ multilayer on top of the normal PSS/PAH multilayer to increase the Nafion content. Permeabilities of the measured membranes for the salt retention and molecular weight cut-off are: 6.2 ± 0.4 , 4.8 ± 0.7 , and $1.7 \pm 0.5 \text{ l} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$ for a PSS, Nafion, and $[\text{Nafion}/\text{PAH}]_6\text{Nafion}$

terminated $[\text{PSS}/\text{PAH}]_8$ multilayer. The salt retentions for NaCl , Na_2SO_4 , MgCl_2 , and MgSO_4 are plotted in **Figure 3.4** for the mentioned PEM membranes.

Figure 3.4: Salt retention towards NaCl , Na_2SO_4 , MgCl_2 , and MgSO_4 for a $[\text{PSS}/\text{PAH}]_8\text{PSS}$ (black bar), $[\text{PSS}/\text{PAH}]_8\text{Nafion}$ (grey bar), and $[\text{PSS}/\text{PAH}]_8 [\text{Nafion}/\text{PAH}]_6\text{Nafion}$ multilayer (white bar). Error bars: standard deviation; $n \geq 3$.

The retention was measured for the listed types of salts to study the retention properties of the membranes towards monovalent and divalent cations and anions. What can be observed in **Figure 3.4**, is that the PSS terminated multilayer shows a typical Donnan exclusion mechanism, with high retentions towards divalent cations (MgCl_2) and low retentions towards divalent anions (Na_2SO_4). [11] This could indicate that the bulk of the multilayer is positively charged and dominates ion retention. It is known for PSS/PAH multilayers that PAH is overcompensating in the multilayer [37] and in addition, when the multilayer is PSS terminated, PAH is highly charged in the bulk of the multilayer. [38, 39] Retention towards NaCl slightly increases from 55% to 65%, when the Nafion content is increased. Furthermore, retention towards MgCl_2 and MgSO_4 slightly change, but remain high with values around 98%. On the other hand, retention towards Na_2SO_4 is low (around 38%) for PSS terminated multilayer and decreases slightly when terminated with Nafion. Although, Nafion influences the hydraulic resistance and hydration of the multilayer greatly, it is observed that the main separation principle for ions, the Donnan exclusion mechanism, is clearly not so much affected by the densification of terminating by Nafion.

Table 3.2: Molecular weight cut-off ($\text{g}\cdot\text{mol}^{-1}$) of PEM membranes with a $[\text{PSS}/\text{PAH}]_8\text{PSS}$, $[\text{PSS}/\text{PAH}]_8\text{Nafion}$, and $[\text{PSS}/\text{PAH}]_8[\text{Nafion}/\text{PAH}]_6\text{Nafion}$ multilayer as an active layer. MWCO was tested by permeating poly(ethylene glycol) with molecular weights of; 200, 400, 600, 1000, and 1500 $\text{g}\cdot\text{mol}^{-1}$ through the membrane. Error bars: standard deviation; $n \geq 3$.

	Molecular weight cut-off ($\text{g}\cdot\text{mol}^{-1}$)
$[\text{PSS}/\text{PAH}]_8\text{PSS}$	301 ± 5
$[\text{PSS}/\text{PAH}]_8\text{Nafion}$	287 ± 8
$[\text{PSS}/\text{PAH}]_8[\text{Nafion}/\text{PAH}]_6\text{Nafion}$	258 ± 15

A well-established method to determine how well membranes separate on size is to measure by means of MWCO experiments. With this method, poly(ethylene glycol) (PEG) molecules with various molecular weights are filtered through the membrane and their retentions are determined by gel permeation chromatography (GPC).[40, 41] In this study, we use PEG molecules with molecular weights of 200, 400, 600, 1000, and 1500 $\text{g}\cdot\text{mol}^{-1}$. The results are shown in **Table 3.2** and the original sieving curves of the MWCO experiments are given in **Figure S3.1** in the supplementary information. From **Table 3.2**, it can be seen that a PSS terminated multilayer has a MWCO of 301 $\text{g}\cdot\text{mol}^{-1}$, when the multilayer is Nafion terminated, the MWCO drops to 287 $\text{g}\cdot\text{mol}^{-1}$. Moreover, when a $[\text{Nafion}/\text{PAH}]_6\text{Nafion}$ multilayer is constructed on top of the original PSS/PAH multilayer, the MWCO drops to a value of 258 $\text{g}\cdot\text{mol}^{-1}$. This indicates that an increasing amount of Nafion in the PEM creates a denser multilayer.

Subsequently, with the knowledge obtained in the previous sections about the multilayer characterization and the membrane performance measurements, we can move on towards our actual goal of retaining difficult-to-remove micropollutants. Furthermore, retaining these small micropollutants gives even more insight into the separation principles of our fabricated PEM membranes. For the micropollutant retention measurement, a cocktail is used of various small micropollutants, varying in charge and molecular weight, as shown in **Figure 3.5**. Many of these micropollutants are chosen based on the most frequently encountered and urgent accumulating micropollutants in our water cycle. [1] In addition, phenolphthalein and bromothymol blue are added to the cocktail to create a mix that covers a wide range of molecular weights and charges.

Figure 3.5: Micropollutant retention at equal flux ($5.5 \text{ l} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$) for PSS (black column), Nafion (grey column), and [Nafion/PAH]₆Nafion (white column) terminated [PSS/PAH]₈ PEM membranes. Micropollutants are sorted by charge, positive to negative from left to right. Retention was measured of a cocktail of micropollutants with a concentration of $3 \text{ mg} \cdot \text{l}^{-1}$ per micropollutant at a pH of 5.8. Error bars: standard error; $n=5$.

In order to compare each PEM membrane fairly, micropollutant retention is measured at equal permeate flux. In addition, to ensure that adsorption is not included in the measured membrane retention, tests were performed after filtering the micropollutant solution for at least 24 hours. [42] Subsequently, the permeate is collected and further analyzed by HPLC to detect any micropollutants in the permeate, these results are plotted in **Figure 3.5**. Here, it can be observed that all multilayers show a complete removal of bromothymol blue ($624 \text{ g} \cdot \text{mol}^{-1}$), this clearly shows that our membranes are defect-free. The PSS terminated multilayer shows a high retention towards the positively charged atenolol, most likely due to excess PAH present inside the PSS/PAH multilayer as described earlier. For this reason, positively charged species are rejected from the bulk of the membrane even though the multilayer is terminated by the negatively charged PSS. Overall, the [PSS/PAH]₈PSS multilayer performs already very well in retaining these small micropollutants when compared to commercial alternatives. [43, 44] This multilayer already has an overall retention of 87% and retentions above 90% for atenolol, atrazine, bisphenol A, and phenolphthalein. However, retention towards bezafibrate, naproxen, and especially SMX can still be greatly improved by making the multilayer denser.

Terminating the multilayer by a single layer of Nafion results in an increased retention towards atrazine (97% to 99%), bisphenol A (94% to 99.5%), sulfamethoxazole (SMX) (52% to 72%), naproxen (69% to 81%), and bezafibrate (88% to 99%) for a [PSS/PAH]₈Nafion in comparison with a [PSS/PAH]₈PSS multilayer at equal permeate flux. Overall, the retention for the tested micropollutants increases from 87% to 93% – doubling membrane selectivity – by adding just a single layer of Nafion. This is in line with the ellipsometry results discussed earlier where we showed that the multilayer becomes denser.

When a [Nafion/PAH]₆Nafion multilayer is built on top of the [PSS/PAH]₈ multilayer, thereby increasing the Nafion content of the multilayer, micropollutant retentions increase overall from 93% to 97% in comparison to a [PSS/PAH]₈Nafion multilayer. An increase in overall retention from 93% to 97% might seem small, but it means that micropollutant permeation through the membrane is reduced by a factor 2. Thus, the effective selectivity of the membrane is doubled as these retentions are obtained at equal flux. When the [Nafion/PAH]₆Nafion multilayer is compared to the [PSS/PAH]₈PSS, overall retention increases from 87% to 97%. This means that 77% less micropollutants permeate the membrane and that the effective selectivity for water to MPs is quadrupled as a result of this high Nafion content. Especially, high increases in retentions are observed for SMX and naproxen, however, it is noticed that the retention towards atenolol and phenolphthalein decreases slightly. Overall, it can be observed that an increasing Nafion content within the multilayer ensures that small and difficult-to-remove micropollutants are retained to a much higher degree. This is completely in line with the layer densification observed on model surfaces (**Figure 3.1**) and membranes (**Figure 3.2**).

In comparison to commercial NF and reverse osmosis (RO) membranes, the PSS terminated membranes fabricated in this study have permeabilities comparable to commercial NF membranes whereas the Nafion terminated membranes have permeabilities in the RO regime. Literature reports retentions towards bisphenol A in the range of 11% to 99% and SMX retentions of 70% to 96% depending on which type of RO membrane is used. [43-45] The PSS/PAH/Nafion membranes produced in this study have retentions higher than 99% towards bisphenol A and between 72% to 97% towards SMX depending on the amount of Nafion used in the PEM membranes. These retention values are consistently higher than the retentions reported in literature. Moreover, we reach these retentions on the basis of Layer-by-Layer assembly, which has considerable advantages such as easy application on the inner surface of hollow fiber membranes and easy upscaling, although the technique is laborious like many other dip-coating techniques. We

have shown that a PSS/PAH membrane formed via this method has already high micropollutant retentions, and that we can improve these properties by densifying the layer with Nafion.

3.4 Conclusions

In this study, we show that by simply terminating a PSS/PAH polyelectrolyte multilayer (PEM) with Nafion, properties of the PEM membrane can be changed. By using Nafion, a polymer commonly used for making ion exchange membrane, the selectivity towards small and difficult-to-remove micropollutants can be greatly enhanced. On silicon wafers, which act as model surfaces, we show that the swelling of a PSS/PAH multilayer decreases by 50% when it is terminated by Nafion. Furthermore, the contact angle of the multilayer changes from 30° to 60° to around 95°. This means that the hydrophobic character of Nafion determines the properties of the multilayer, making it less hydrated and more hydrophobic. This change in multilayer properties can be directly connected to the performance of the membrane.

The molecular weight cut-off (MWCO) goes down from 301 g·mol⁻¹ to 258 g·mol⁻¹ when the Nafion content of the PSS/PAH/Nafion multilayer increases. Furthermore, the hydraulic resistance of the membrane towards water is doubled when the multilayer is terminated by a single layer of Nafion and increases even more when the Nafion content is increased. This is in line with the observed decrease in swelling, and in combination with the lowering MWCO, this directly translates in an overall retention towards small and difficult-to-remove micropollutants (200 to 650 Dalton) that increases from 87% to 97%. This means that the selectivity of the membrane is quadrupled, while the same salt retentions are maintained. A sharp increase in retention was observed especially for bisphenol A, sulfamethoxazole, naproxen, and bezafibrate when the Nafion content was introduced and increased. Comparing micropollutant retention with reported literature values, the membranes produced in this study show higher retention values. This work shows that PEM membranes can be optimized towards a high micropollutant retention, in which low hydration of the multilayer plays an important role. This knowledge can be used to further optimize PEM membranes for micropollutant removal.

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3.6 Supplementary Information

3.6.1 Molecular weight cut-off sieving curves

Figure S3.1: Sieving curves of the MWCO measurements of PSS/PAH]₈PSS (black line), [PSS/PAH]₈Nafion (dashed line), and [PSS/PAH]₈⁻/[Nafion/PAH]₆Nafion (grey line) membranes as function of the molecular weight of a PEG molecule.

3.7 References

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Chapter 4

Asymmetric Polyelectrolyte Multilayer Membranes with Ultrathin Separation Layers for Highly Efficient Micropollutant Removal

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Abstract

New membrane materials are urgently needed to address the increasing concentrations of harmful organic micropollutants (e.g. pharmaceuticals, pesticides and plasticizers) in our surface and drinking water. Currently, the densest available membranes can remove micropollutants sufficiently, but only at very low permeabilities and by producing a highly saline, difficult to treat waste stream. We improve permeability 5-10 fold by producing an asymmetric polyelectrolyte multilayer (PEM) on a porous membrane, with a separation layer thickness of only 4 nm. This is achieved by first coating an open multilayer to prevent defects, and subsequently a thin and dense multilayer. This novel membrane shows a very high (98%) retention towards a mix of common micropollutants. Moreover, it only retains 10-15% of NaCl, preventing the formation of a saline waste stream. A detailed literature study shows that the asymmetric PEM membrane, with this unique combination of properties, significantly outperforms commercial membranes for micropollutant removal applications.

4.1 Introduction

The emergence of small organic molecules (100-1000 Dalton) from medicines, pesticides and plasticizers (micropollutants) in wastewater and surface water is a significant challenge that demands for new and specially designed membrane materials [1,2,3]. Growing welfare and world-population lead to increasing micropollutant concentrations in surface waters and drinking water sources, threatening both the aquatic environment and drinking water quality.

Current technologies are unable to efficiently remove these micropollutants from wastewater and surface water streams. Adsorption, for example, is not sufficient to remove micropollutants for more than 90% [4]. Membrane technologies are more promising, as many commercial reverse osmosis (RO) membranes do remove >90% of micropollutants, but operating these membranes is very energy-consuming because of their low water permeabilities ($1\text{--}2\text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$ for modern RO membranes) [5]. Commercial nanofiltration (NF) membranes are more open, but with increasing permeability, comes lower retentions, especially towards small and uncharged micropollutants such as bisphenol A [6,7]. The effectiveness of currently available membranes is therefore limited. Moreover, RO and tight NF membranes were designed for desalination and can only remove micropollutants together with ions [8]. This can lead to a product stream where salts need to be re-added to make the water suitable for agriculture or human consumption. Even more problematic is the creation of highly saline micropollutant waste streams, that are complex and expensive to treat [9,10].

Polyelectrolyte multilayers (PEMs) are promising materials to help solve this problem. PEMs can be coated on surfaces, including porous membrane supports, under mild and aqueous conditions by alternately exposing the substrate to polycation and polyanion solutions. During each of these steps, electrostatic interactions lead to the formation of a thin (0.5-5 nm) polyelectrolyte layer on top of the previous, oppositely charged layer [11,12,13]. Previous research shows that such layers show a high stability when used as dense separation layers on a charged membrane support, being resistant against repetitive backwashing [14]. The strength of this approach is that the properties of the PEM can be finely tuned, for example by the number of layers and the salt concentration and pH during the coating process [13,15]. Additionally, a large variety of polyelectrolytes can be used to determine the properties of the layer [15,16]. Hence, PEM based membranes can be optimized towards specific applications including desalination [17] and ion separation [18]. Moreover, PEM coatings can be easily applied on hollow fiber membranes, that have

significant advantages over other membrane geometries such as reduced fouling, which eliminates the need for pretreatment [19].

Their largest advantage, however, is their potential to form very thin separation layers. Since the early days of membrane usage, the active separation layers of membranes have become thinner and thinner to increase permeability and thus decrease energy demand. One of the most important breakthroughs in this regard was the introduction of membranes with an asymmetric pore distribution [20,21], consisting of a thin active separation layer with a small pore size and a supporting layer with a larger pore size to provide mechanical stability without unnecessarily reducing water permeability.

Unfortunately, when coating a few nanometers thin PEM on a porous support, it will not completely close the pores (**Figure 4.1A**). A much thicker layer is required to produce a defect-free membrane. Moreover, once the pores are filled, the effective thickness of the PEM layer is much higher than the coated thickness because permeating water has to travel a long pathway through the filled pores (**Figure 4.1B**). As a consequence, the potential of PEMs to form ultrathin separation layers cannot be fully exploited and the pure water permeability of PEM based membranes is still relatively low.

Here we introduce a unique approach that improves separation properties by taking membranes to the next level of asymmetry. To maintain high water permeability, we close the support pores with a relatively open, permeable PEM, and subsequently coat a thin, dense PEM on top of the first layer to generate high selectivity (**Figure 4.1C**). We will demonstrate that this approach allows us to make membranes with separation layers as thin as 4 nm.

4.2 Materials and Methods

4.2.1 Chemicals

Poly(styrene sulfonate) (PSS, 200 kDa, 30 wt.% in water) and poly(acrylic acid) (PAA, 250 kDa, 35 wt.% in water) were obtained from Sigma Aldrich. Poly(allylamine hydrochloride) (PAH, 150 kDa, 40 wt.% in water) was obtained from Nittobo Medical, Japan. Sodium chloride was obtained from AkzoNobel, The Netherlands, Sodium sulphate from Merck and sulfamethoxazole from Fluka. All other chemicals were obtained from Sigma Aldrich.

4.2.2 Reflectometry

Reflectometry was performed as described by de Grooth et al. 2014 [50]. Polyelectrolyte solutions as well as the rinsing solution contained 50 mM NaCl; PAH and PAA solutions were adjusted to pH 6. Adsorption was calculated with the following values: $dn/dc_{PAH} = 0.21$ mL/g, $dn/dc_{PSS} = 0.18$ mL/g, $dn/dc_{PAA} = 0.16$ mL/g [51]. The corresponding Q-factors are 26 for PAH, 30 for PSS and 34 for PAA.

4.2.3 Layer-by-layer PEM coating

Polyelectrolyte multilayers were coated on a porous hollow fiber nanofiltration support (tight positively charged nanofiltration membranes, 90% MWCO 10 kDa, inner diameter 0.7 mm, NX Filtration, The Netherlands). The membranes were first rinsed in 50 mM NaCl solution before being completely immersed for 15 minutes in the first polyelectrolyte solution (PSS). After each polyelectrolyte coating step, the membranes were rinsed 3x 5 minutes in 3 subsequent 50 mM NaCl solutions. All polyelectrolyte solutions contained 0.1 g/L of polyelectrolyte and 50 mM NaCl. PAA and PAH solutions were adjusted to pH 6.0. To produce asymmetric membranes, membranes were rinsed twice after the last PSS/PAH coating step and the entire process was started over for PAA/PAH with separate polyelectrolyte and rinsing solutions.

All membranes were coated with 10.5 polyelectrolyte bilayers in total. As a result of the complete immersion in the polyelectrolyte and rinsing solutions, both the inner and outer surface of the hollow fibers are coated with the PEM. However, because the membranes have a much smaller pore size at the inner surface, only at this surface a defect-free separation layer will be formed.

After the last rinsing steps in 50 mM NaCl, they were rinsed in demineralized water and incubated in 15 wt.% glycerol solution for at least 4 hours. The membranes were

subsequently dried o/n and single membranes were potted in 18 cm long modules for characterization.

4.2.4 Membrane characterization

Membranes were characterized using a crossflow setup operated by a rotary vane pump (BN71B4 pump motor, Bonfiglioli, Italy; IMTI 1.5M inverter, Electroil, Italy; PA411 pump head, Fluid-o-Tech, Italy). Pure water permeability was determined at 4.5 bar (average pressure over each membrane) and a flow of 5 L/h per module. Salt retentions were determined at an average pressure of 1.7 bar and a flow of 10 L/h per module. Feed and permeate salt concentrations were measured by conductivity.

Molecular weight cutoff was determined with a feed mixture of ethylene glycol, PEG200, PEG400, PEG600, PEG1500 and PEG2000, 1 g/L each. Again, the crossflow setup was operated at 1.7 bar and a flow of 10 L/h per module; only for the 10.5 bilayer PAA/PAH membranes, the crossflow setup was operated at 4.8 bar to create a membrane flux more comparable to the other membranes. Feed and permeate samples were analyzed via GPC (Agilent 1200/1260 Infinity GPC/SEC series, Polymer Standards Service data center and column compartment) over two Polymer Standards Service Suprema 8x300 mm columns in series: 1000 Å, 10 µm followed by 300 Å, 10 µm. Concentrations were determined via refractive index detection.

For measuring micropollutant retentions, a cocktail was prepared containing 3 mg/L of each of the micropollutants (atenolol, atrazine, bezafibrate, bisphenol A, bromothymol blue, naproxen, phenolphthalein and sulfamethoxazole) and adjusted to pH 5.8. Again, the crossflow setup was operated at 1.7 bar and a flow of 10 L/h per module. The separation process was allowed to stabilize o/n while leading permeate back into the feed. Subsequently around 2 mL of permeate was collected from each module and a calibration range was prepared from the feed. All samples were analyzed by UHPLC (Dionex Ultimate 3000, water/acetonitrile, 0.1% phosphoric acid) over a Thermo Scientific Acclaim RSLC 120 C18 column (2.2 µm, 2.1x100 mm) and micropollutant concentrations were determined via UV/Vis detection at 225 nm, bromothymol blue at 430 nm.

4.2.5 Ellipsometry

Silicon wafers were treated with an oxygen plasma and subsequently dip coated with 4 bilayers of PSS/PAH (starting with PAH) and 0, 1, 2 or 3 bilayers of PAA/PAH. The dip coating procedure was identical to the dip coating of hollow fiber membranes. After the last layer, the wafers were still rinsed twice in 50 mM NaCl and stored in demineralized

water. Ellipsometry was performed with a rotating compensator ellipsometer (Mk-2000V, J.A. Woollam Co., Inc.) in a wavelength range of 370-1000 nm. Wet PEM thickness was measured in a liquid cell with demineralized water at a 75° angle of incidence, at room temperature. After the wet measurements, the wafers were dried under nitrogen flow and analyzed by again under ambient conditions, at three different angles of incidence (65, 70, and 75°).

Data were fitted with CompleteEase software, using a Cauchy model. The polyelectrolyte multilayer was modeled as a single layer. For the wet measurements, both refractive index and layer thickness were fitted, because the refractive index strongly depends on the hydration. Dry thickness was fitted with a fixed refractive index of 1.49 [52].

4.2.6 Scanning electron microscopy

Non-coated hollow fiber membranes and [PSS/PAH]_{8.5}+ [PAA/PAH]₂ membranes were incubated o/n in demineralized water and then incubated for 1 hour in subsequently 25% isopropanol, 50% isopropanol, 75% isopropanol, 100% isopropanol, 25% n-hexane in isopropanol, 50% n-hexane in isopropanol, 75% n-hexane in isopropanol, and 100% n-hexane (percentages in vol%). The membranes were then dried under ambient conditions.

The membranes were prepared for cross-section imaging by freezing them in liquid nitrogen and breaking them. Membrane pieces were then glued on a sample holder with conductive silver paint and dried in a vacuum oven at 30 °C. The samples were sputter-coated with 5 nm platinum-palladium and then imaged in a JEOL JSM-7610F field emission scanning electron microscope.

4.2.7 Physical membrane stability

To perform the stability test, 9 PAH/PSS bilayers and 2 PAH/PAA bilayers were coated on tight negatively charged nanofiltration membranes (90% MWCO 10 kDa, inner diameter 0.6 mm, NX Filtration, The Netherlands), as described earlier but starting with the polycation (PAH) instead of the polyanion. These membranes were dried, potted and characterized as earlier mentioned. Subsequently, the membranes were incubated in 3M NaCl, pH 3 (HCl) for 24h. After rinsing with demineralized water, they were characterized again.

4.3 Results and Discussion

An essential part in the design of an asymmetric PEM coating is the choice of polyelectrolytes. From previous studies we know that poly(acrylic acid)/poly(allylamine hydrochloride) layers (PAA/PAH), coated at pH 6 and terminated with a PAA layer, form dense PEMs with 60-80% retention of both charged and neutral micropollutants [22]. However, these retentions were achieved at the low water permeability of $1.8 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$, in line with expectations (**Figure 4.1B**). PEM membranes prepared with other polyelectrolytes can have much higher permeabilities. For example, membranes based on poly(styrene sulfonate) (PSS)/PAH, terminated with PSS, have a permeability of 13-16 $\text{L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ after pore closure (supplementary **Figure S4.1**). Moreover, PSS and PAH form very stable multilayers with a low polyelectrolyte mobility [23]. A good micropollutant removal membrane requires the permeability and stability of PSS/PAH layers, but the selectivity of PAA/PAH layers.

Figure 4.1. Concept of asymmetric PEM membranes. a: Coating a thin dense layer on a porous support will lead to defects; b: if the support pores are filled with a dense PEM with good separation properties, water needs to travel a long pathway through the PEM and the water permeability will be low; c: if the support pores are filled with an open PEM, and a thin layer of dense PEM with the desired separation properties is coated on top, a combination between a high selectivity and permeability can be achieved.

Producing asymmetric PEM membranes with a PSS/PAH bottom layer and a thin PAA/PAH top layer is therefore a promising option to fully benefit from the high stability and permeability of the first polyelectrolyte pair and the selective properties of the latter.

Indeed, we find that building such layers on model surfaces is a straightforward process (supplementary **Figure S4.2**). To demonstrate the potential of such asymmetric layers, five types of hollow fiber membranes were prepared, each with 10.5 bilayers in total. This includes two control membrane types that are coated completely with either PSS/PAH or PAA/PAH ([PSS/PAH]_{10.5} and [PAA/PAH]_{10.5}), and three asymmetric membrane types [PSS/PAH]_{8.5}+ [PAA/PAH]₂, [PSS/PAH]_{7.5}+ [PAA/PAH]₃ and [PSS/PAH]_{6.5}+ [PAA/PAH]₄. All membranes are terminated with the polyanion, because we previously found that PAA-terminated PAA/PAH layers show higher micropollutant retentions than PAH-terminated ones [22].

Of the five different membrane types, we determined pure water permeability and molecular weight cutoff, MWCO (**Figure 4.2A**). The permeability of the PSS/PAH membranes is 15.2 Lm⁻²h⁻¹bar⁻¹, while for PAA/PAH it is only 1.4 Lm⁻²h⁻¹bar⁻¹, showing the clear difference in permeability between a dense and a more open PEM coating. The asymmetric membranes have significantly higher permeabilities than the PAA/PAH membranes, up to 12.8 Lm⁻²h⁻¹bar⁻¹ for the [PSS/PAH]_{8.5}+ [PAA/PAH]₂ membranes. While the permeability keeps on decreasing with an increasing number of PAA/PAH layers, the 90% MWCO plateaus around 240 Da for the asymmetric membranes. These results already demonstrate the promise of these asymmetric membranes, showing that we can decrease the MWCO by coating PAA/PAH on top of PSS/PAH layers, while retaining a permeability close to the much more open PAH/PSS multilayer. Surprisingly we found a very high 90% MWCO for the 10.5 bilayer PAA/PAH membranes. For a better comparison, supplementary **Figure S4.3** shows the full sieving curves of our membranes, where we can see that the [PAA/PAH]_{10.5} membranes actually perform better than the others in the low molecular weight range. The poor 90% MWCO performance of these membranes indicates that they suffer from small defects; we elaborate on this in **Figure S4.3**.

Figure 4.2. Performance of the asymmetric and control membranes. a: Pure water permeability and molecular weight cutoff; b: micropollutant and NaCl retention. Error bars: standard error; $n=4$.

Although the obtained MWCO results give a good indication that our asymmetric membranes could retain micropollutants, it is critical to prove this by measuring real micropollutant retentions. For this purpose we use a micropollutant mix with 8 micropollutants, containing positively charged, negatively charged and neutral organic molecules, with size varying from 216 to 624 Da. Among them are several pharmaceuticals (atenolol, sulfamethoxazole, naproxen and bezafibrate), a pesticide (atrazine) and a plasticizer (bisphenol A). Structures, molecular weight and pK_a values of the micropollutants can be found in supplementary **Table S4.1**.

The micropollutant retentions show a clear optimum for the asymmetric membranes (**Figure 4.2B**), which is in line with the MWCO results. Moreover, all micropollutant retentions are above 90% for the asymmetric membranes, showing that the asymmetric concept provides an excellent selectivity for water over micropollutants. The dense PAA/PAH top layers reject the micropollutants more effectively than PSS/PAH, but as the PAA/PAH top layer is very thin the water permeability remains high. The asymmetric membranes are even shown to be more selective than a symmetric dense PAA/PAH layer. We expect that the stable PAH/PSS bottom layer helps to prevent defects that would otherwise lower the selectivity. Moreover, in nanofiltration a higher water flux tends to lead to a higher solute retention according to the solution-diffusion model [24], which also explains the optimum in micropollutant retention for the asymmetric membranes.

The differences in retention between the micropollutants seem to be largely dependent on micropollutant size. Bromothymol blue, the largest molecule in the mix, is not detected in

any of the permeates. The other large micropollutants bezafibrate, phenolphthalein and atenolol are retained well by the asymmetric membranes without a clear charge dependency. The smallest micropollutants (atrazine, bisphenol A, sulfamethoxazole and naproxen) are retained slightly less. Differences in retention between those do not correlate to size or charge but could be explained according to the solution-diffusion model by differences in affinity for the PEM.

The low sodium chloride retentions of the asymmetric membranes, only 11-14%, demonstrate even more clearly that size exclusion is the predominant separation mechanism. Sodium chloride ions, with a diameter of 0.2 nm for both Na^+ and Cl^- [25], are much smaller than the micropollutants that typically have dimensions around 1 nm [26] and are therefore retained less. If a charge-based exclusion mechanism would be dominant, no large difference would be expected between the retention of sodium chloride ions and other monovalent species such as the charged micropollutants. Interestingly, the lack of charge exclusion shows that our membranes contain a very low net charge, even though their separation layers consist of polyelectrolytes.

The average micropollutant retentions of all the asymmetric membranes are around 98%. In this region of high retentions, a small change in retention requires a very large improvement in membrane selectivity. From standard PAH/PSS membranes (93% retention) to the asymmetric membranes we observe a 3.5 fold increase in membrane selectivity. Specifically with the $[\text{PSS}/\text{PAH}]_{8.5} + [\text{PAA}/\text{PAH}]_2$ membranes, we can therefore produce water with 3.5 times less micropollutants at only slightly lower fluxes compared with our PSS/PAH control membrane. The asymmetric coating approach clearly leads to much higher selectivities, with just a small reduction in flux. Because of this combination of high selectivity and permeability, we expect that the asymmetric membranes have very thin separation layers. Indeed, by ellipsometry we estimated the 2, 3 and 4 bilayer PAA/PAH separation layers to be only 4, 9 and 16 nm in thickness, respectively, in their hydrated state (supplementary file **S4.5**). The $[\text{PSS}/\text{PAH}]_{8.5} + [\text{PAA}/\text{PAH}]_2$ layers were also visualized by field emission scanning electron microscopy (supplementary **Figure S4.6**), where the dry PEM thickness was found to be around 30 nm, in line with the ellipsometry results.

The estimated 4 nm thickness of the $[\text{PAA}/\text{PAH}]_2$ top layer is incredibly thin, given that common commercial separation layer thicknesses are 0.1-1 μm [24]. Via some procedures it is possible to obtain more homogeneous and thinner layers via interfacial polymerization, down to 25 nm [27] or even 8 nm [28]. To our knowledge, however, our 4 nm separation layer is the thinnest separation layer reported so far by using scalable

technology. Moreover, the asymmetric multilayers are physically stable as incubating them in an acidic salt bath hardly influences permeability and MWCO (supplementary **Figure S4.7**). Besides being readily scalable, asymmetric PEM coating also provides a very easy and environmentally friendly way to produce these extremely thin, defect-free separation layers. This demonstrates the potential of asymmetric PEMs for large-scale applications.

To validate the outstanding properties of our asymmetric membranes, in particular the $[\text{PSS}/\text{PAH}]_{8.5} + [\text{PAA}/\text{PAH}]_2$ membranes, we compared the performance of our membranes with the performance of commercially available reverse osmosis and nanofiltration membranes as described in literature. A detailed overview can be found in supplementary file **S8** in **Table S4.2**. In **Figure 3A**, permeability and micropollutant retention are plotted against each other for our asymmetric PEM membranes (dark symbols), symmetric PEM membranes (grey symbols) and commercially available membranes (white symbols). Where the asymmetric PEM membranes have a consistently high retention for all micropollutants, the commercial membranes tend to work well for only some of the investigated micropollutants, and have low retention for others. The dashed lines show the upper limit for single micropollutant results obtained with commercial membranes. The retentions of our $[\text{PSS}/\text{PAH}]_{8.5} + [\text{PAA}/\text{PAH}]_2$ membranes are above these lines for all micropollutants, which shows that their average performance is even better than the best results for commercial membranes. Dotted lines show the upper limit for bisphenol A as obtained with commercial membranes. Bisphenol A is the most difficult micropollutant to retain, as for the commercial membranes, only the RO membranes retain it for more than 95%. The high retention of our membranes towards all micropollutants, including bisphenol A, thus demonstrates that our asymmetric membranes have a micropollutant retention comparable with or better than the best RO membranes. At the same time, they have a pure water permeability in the range typical for NF membranes.

Figure 4.3. Asymmetric and symmetric PEM membranes in comparison with commercial nanofiltration and reverse osmosis membranes. a: Permeability versus micropollutant retention; b: sodium chloride retention versus micropollutant retention. White symbols: commercial membranes; grey symbols: symmetric PEM membranes in this study; dark symbols: asymmetric membranes in this study. Dashed lines: best single results obtained with commercial membranes; dotted line: best single results obtained with commercial membranes for bisphenol A. If for a single micropollutant different data were obtained in literature with the same commercial membrane, results were averaged. Detailed information can be found in supplementary table S8.

Finally, as shown in **Figure 4.3B** the membranes have a very low sodium chloride retention compared with commercial membranes, in the range of tight ultrafiltration (UF) membranes. The asymmetric PEM coating thus allows us to decouple the usual correlation between permeability, salt retention and micropollutant retention, and improves membrane efficiency beyond the traditional limits. This means that categorization of our new asymmetric PEM based membrane as an NF membrane is not suitable because typically, NF membranes are considered to show average separation properties, in between those of RO and UF membranes. In contrast, our membrane decouples and combines single desirable properties of RO, NF and UF type membranes: high water permeability (NF), high micropollutant retention (RO) and low salt retention (UF). We thus propose that the membrane should be considered the first in a new category, the Chimera membrane, named after the mythical creature that also combined aspects of various different animals into one.

The unique properties of our membranes are further highlighted by their exceptional permselectivity in terms of salt permeation over micropollutant permeation, that is at least one order of magnitude higher than for commercial membranes, as shown in **Figure 4.4** (calculation methods can be found in supplementary file **S9**). Some commercial

membranes show a permselectivity below 1, which means that their salt retention is higher than their micropollutant retention, in strong contrast to the high sodium chloride permeation of the asymmetric PEM membranes. Salt permeation is very beneficial as it will prevent the formation of a highly saline waste stream that is typical for standard RO and NF membranes. Moreover, it avoids buildup of a high osmotic pressure over the membrane, that would demand a higher transmembrane pressure to achieve the same water flux.

Figure 4.4. Pure water permeability versus permselectivity of PEM and commercial membranes. Dark symbols: asymmetric PEM membranes in this study; grey symbols: symmetric PEM membranes in this study; white symbols: commercial membranes. If for a single micropollutant different data were obtained in literature with the same commercial membrane, results were averaged. Calculations are explained in supplementary file S9.

4.4 Conclusions

In summary, our new concept of asymmetric PEM membranes allows us to create advanced membrane materials with ultrathin separation layers and a unique combination of desirable separation properties, allowing its classification in a new membrane category: the Chimera membrane. We have successfully applied this new membrane to achieve an outstanding micropollutant retention (98%) and water permeability ($12.8 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$), thereby outperforming the selectivity of commercial membranes to a large extent. With asymmetric PSS/PAH + PAA/PAH coatings we were able to produce selective layers as

thin as 4 nm, using a highly scalable membrane fabrication approach. An additional benefit of our PEM membranes is their low salt retention, such that NaCl does not accumulate in the micropollutant waste stream. Clearly, our approach to produce asymmetric PEM membranes is highly beneficial for micropollutant removal processes. These membranes are very suitable for the production of safe drinking water and for micropollutant removal from wastewater, but also for other applications such as the separation of salts and organic compounds in biorefinery. Finally, this work provides fundamentally new membrane design principles for improved selectivities that can be tuned to other important applications, including desalination and ion recovery.

4.5 Acknowledgements

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4.6 Supplementary Information

4.6.1 S1 Permeability of PSS/PAH multilayers

Figure S4.1. Permeability and MgSO_4 retention of PSS/PAH coated at 50 mM NaCl, as a function of the number of (PSS-terminated) bilayers. Initially the permeability decreases quickly as the support pores are becoming smaller. After 4.5 bilayers, this trend changes towards a slower and linear decline, which shows that the pores are closed and the permeability only depends on total layer thickness. Simultaneously, the magnesium chloride retention shows its maximum increase which also indicates pore closure. After 6.5-9.5 bilayers, where the pores are closed and MgSO_4 retention reaches its maximum, the permeability is 13-16 $\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$. Error bars: standard error; $n=4$.

4.6.2 S2. Optical reflectometry of PSS/PAH + PAA/PAH layer buildup

Figure S4.2. Adsorption of PSS/PAH and PAA/PAH (8 monolayers each) onto a plasma-treated silicon oxide surface. For PAH/PSS a linear growth profile is observed, that changes to a more exponential growth profile when switching to PAA/PAH. This demonstrates that asymmetric PEM layers can be successfully grown, with PAA/PAH having its expected growth profile even when grown on top of a PAH/PSS multilayer. Error bars: standard error; $n=3$.

4.6.3 S3. MWCO sieving curves

Figure S4.3. Sieving curves of the symmetric and asymmetric membranes, showing the relative permeate concentration (sieving coefficient) of differently sized PEG molecules as determined by GPC. The PSS/PAH and asymmetric membranes show a trend towards a lower MWCO with increasing PAA/PAH layer thickness. The 10.5 bilayer PAA/PAH membranes show a deviating behavior, with the best retentions for molecular weights below 150 Da, but an apparent leakage of large size PEG molecules. The unexpectedly high 90% MWCO that follows from these results (1083 ± 64 Da, figure 2a) can be explained by the presence of defects in the multilayer, leading to a small convective flow that drags a percentage of the PEG molecules with it. This has the largest relative impact on the retention of molecules that would otherwise be retained almost 100%, and leads to plateauing of the curve towards a sieving coefficient higher than 0. It thus seems that the PAA/PAH membranes in theory could be our densest membranes with the lowest MWCO, in line with the trend observed for the other membranes, but that they have defects. Therefore, another advantage of the asymmetric membranes is that the PSS/PAH bottom layer seems to prevent defect formation.

4.6.4 S4. Micropollutants

Table S4.1. Structure, molecular weight and pK_a values of the micropollutants used in this study

Micro-pollutant	Chemical structure	Mw (Da)	pK _{a,acidic} ^[a]	pK _{a,basic} ^[a]
atenolol		266.34	14.1	9.67
atrazine		215.69	14.5	4.2
bezafibrate		361.82	3.84	-
bisphenol A		228.29	9.78	-
bromothymol blue		624.38	8.41	-
naproxen		230.26	4.19	-

phenolphthalein		318.32	9.16	-
sulfamethoxazole		253.28	6.16	1.97

[a] pK_a values obtained from ChemAxon

4.6.5 S5. PAA/PAH separation layer thickness

We performed ellipsometry to estimate the separation layer thickness of our asymmetric membranes. However, the wet thickness of a thin PAA/PAH top layer on a PSS/PAH bottom layer can't be measured directly, because the hydration of the entire PEM, and therefore also the thickness of the bottom layer, decreases when more layers are coated on top. This is visible in **Figure S4.4A** as the difference in wet and dry thickness decreases by adding more PAA/PAH layers. Thus, only the dry PAA/PAH thickness can be directly calculated from the total layer thickness and the PSS/PAH bottom layer thickness. However, using the wet and dry thickness of the entire multilayer, we can calculate the swelling of the layer:

$$\text{swelling} = (\text{wet thickness} - \text{dry thickness}) / \text{dry thickness} \quad (4.1)$$

Assuming that the PAA/PAH layer swells as much as the entire multilayer, we use this swelling value and the same equation to subsequently calculate the wet thickness of the PAA/PAH layer from its dry thickness. **Figure S4.4B** shows this estimated hydrated thickness of the PAA/PAH layers, which is only 4 nm for our thinnest separation layer (2 PAA/PAH bilayers).

Figure S4.5a. Wet and dry thickness of a reference PSS/PAH multilayer and PSS/PAH multilayers with 2, 3 or 4 bilayers of PAA/PAH coated on top, measured by ellipsometry. Error bars: standard error; n=3.

Figure S4.5b. Estimated wet thickness of the PAA/PAH top layer. Error bars: standard error; n=3.

4.6.6 S6. Scanning electron microscopy

Figure S4.6. Cross-section scanning electron microscopy images of the inner surface of the uncoated support membrane (left) and the $[\text{PSS}/\text{PAH}]_{8.5} + [\text{PAA}/\text{PAH}]_2$ membrane (right). The polyelectrolyte multilayer on top of the support membrane is clearly visible and around 30 nm in thickness. Regarding the linear growth of the PSS/PAH layer, this is in good agreement with the dry thicknesses measured by ellipsometry, from which a layer thickness of 26 nm would be expected for 8.5+2 bilayers PSS/PAH+PAA/PAH. The PSS/PAH and PAA/PAH layers however, as expected, can not be distinguished.

4.6.7 S7. Physical stability of the PSS/PAH + PAA/PAH multilayer membrane

Figure S4.7. Pure water permeability and MWCO of the asymmetric membranes before and after 24h incubation in a 3M NaCl bath, pH 3. Charge-charge interactions are expected to be severely destabilized by ionic screening and PAA protonation under these circumstances. Nevertheless the membrane properties are hardly influenced by this treatment: the MWCO increased only marginally and water permeability even went down slightly. This demonstrates that the PEM was not disintegrated under these harsh conditions. Consequently, an excellent physical stability of the asymmetric PEM can be expected when operated under normal conditions (neutral pH and mM-range salt concentrations). Error bars: standard error; n=5.

4.6.8 S8. Literature studies of micropollutant removal by commercial and PEM membranes

Table S4.2a. Overview of micropollutant removal in literature and this study.

Author	Membrane	Material	Manufacturer	PWP (Lm ⁻² h ⁻¹ bar ⁻¹)	Process conditions	NaCl Retention (%)
Fujioka et al. 2014 [29]	NF90	polyamide TFC	Dow Filmtec	-	10 bar, flux 20 Lm ⁻² h ⁻¹	81
				-		
				-		
				-		
	NF270	polyamide TFC	Dow Filmtec	-	10 bar, flux 20 Lm ⁻² h ⁻¹	16
				-		
				-		
				-		
Xu et al. 2005 [30]	NF200	polyamide TFC	Dow Filmtec	5.0	crossflow 7.3 L/min, 2.4 Jo/k	-
	NF90	polyamide TFC	Dow Filmtec	10.4	crossflow 7.3 L/min, 1.9 Jo/k	93
	XLE	polyamide TFC	Dow Filmtec	9.0	crossflow 7.3 L/min, 2.4 Jo/k	99
	TFC-SR2	polyamide TFC	Koch	18.1	crossflow 7.3 L/min, 2.4 Jo/k	-
	TFC-HR	polyamide TFC	Koch	3.5	crossflow 7.3 L/min, 1.3 Jo/k	99
Kimura et al. 2003 [31]	ESNA	polyamide TFC	Hydranautics	7.8	5.52 bar, average flux 10.0 mL/min	-
	XLE	polyamide TFC	Dow Filmtec	9.2	5.52 bar, average flux 11.8 mL/min	99
Kimura et al. 2004 [32]	XLE	polyamide TFC	Dow Filmtec	3.94	5 bar, average flux 1.05 mL/min	90
				3.94		90
	SC-3100	cellulose acetate	Toray	1.31	5 bar, average flux 0.35 mL/min	94
				1.31		94
Yüksel et al. 2013 [33]	AD	polyamide TFC	GE osmonics	0.85	10 bar, crossflow 1.6 L/min	-
	CE	cellulose acetate	GE osmonics	2.41		97
	XLE	polyamide TFC	Dow Filmtec	5.91		99
	NF270	polyamide TFC	Dow Filmtec	14.86		80
	NF90	polyamide TFC	Dow Filmtec	6.05		93
	BW30	polyamide TFC	Dow Filmtec	1.97		99
Bolong et al. 2010 [34]	PES-	polyethersulfone	-	11.08	5.51 bar, crossflow velocity 0.4–0.5 m/s	52
	PEGHBS					

Comerton et al.	NF270	polyamide TFC	Dow Filmtec	15.5	3.45 bar, crossflow velocity 0.8 m/s	80
2008 [35]	"	"	"	15.5	10.34 bar, crossflow velocity 0.8 m/s	80
	TS80	polyamide TFC	TriSep	4.5	10.34 bar, crossflow velocity 0.8 m/s	-
	"	"	"	4.5	10.34 bar, crossflow velocity 0.8 m/s	-
	X20	polyamide TFC	TriSep	2.5	10.34 bar, crossflow velocity 0.8 m/s	99
"	"	"	"	2.5	10.34 bar, crossflow velocity 0.8 m/s	99
Simon et al.	TFC-SR2	polyamide TFC	Koch	-	crossflow velocity 30.4 cm/s, flux 54 Lm ⁻² h ⁻¹	10
2009 [36]	NF270	polyamide TFC	Dow Filmtec	-		45
	NF90	polyamide TFC	Dow Filmtec	-		85
	BW30	polyamide TFC	Dow Filmtec	-		98
Simon et al. 2012 [37]	NF270	polyamide TFC	Dow Filmtec	-		27
Chang et al. 2012 [38]	NF270	polyamide TFC	Dow Filmtec	11	6.9 bar, crossflow velocity 0.3 m/s	80
	NTR7450	sulfonated PES	Nitto Denko	12		-
Verliefde et al. 2008 [39]	TS80	polyamide TFC	TriSep	4.3	crossflow velocity 0.2 m/s	-
				4.3		-
	Desal HL	polyamide TFC	GE osmonics	7.2	crossflow velocity 0.2 m/s	-
Ge et al. 2017 [40]	NF270	polyamide TFC	Dow Filmtec	-	5 bars	52
				-		52
				-		52
Dang et al. 2014 [41]	NF270	polyamide TFC	Dow Filmtec	11	crossflow velocity 30.4 cm/s, Flux 42 Lm ⁻² h ⁻¹	80
				11		80
Zhang et al. 2004 [42]	Desal HL	polyamide TFC	GE osmonics	9.0	8 bar, crossflow 700 L/h	-
	Desal DL	polyamide TFC	GE osmonics	5.5		-
	UTC-20	polyamide TFC	Toray	10.8		-
	UTC-60	polyamide TFC	Toray	4.2		-
Caus et al. 2009 [43]	Desal HL	polyamide TFC	GE osmonics Microdyn-Nadir	10.5	8 bars	55
	N30F	polyethersulfone	Nadir	5.6		53
	NF270	polyamide TFC	Dow Filmtec	11.5		85
Azaïs et al. 2016 [44]	NF90	polyamide TFC	Dow Filmtec	6.6	2 bar, crossflow velocity 0.5 m/s	88
	NF270	polyamide TFC	Dow Filmtec	14.1		56
Yangali et al. 2009 [45]	NF200	polyamide TFC	Dow Filmtec	4.2	2.8 bar, crossflow velocity 0.38 cm/s	-
				4.2		-
				4.2		-

	NF90	polyamide TFC	Dow Filmtec	4.2 9.3	2.8 bar, crossflow velocity 0.38 cm/s	- 93
				9.3 9.3 9.3		93 93 93
Xie et al. 2012 [46]	FO	cellulose triacetate	Hydration Tech Innovation	1.1	10 bar, crossflow velocity 25 cm/s	93
This study	PES	PSS/PAH 10.5 bilayers	50 mM NaCl, pH 6	15.2	1.7 bar, crossflow velocity 7.2 m/s	16
	"	"	"		"	
	"	"	"		"	
	"	"	"		"	
	"	"	"		"	
	PES	PAA/PAH 10.5 bilayers	50 mM NaCl, pH 6/6	1.4	1.7 bar, crossflow velocity 7.2 m/s	5
	"	"	"		"	
	"	"	"		"	
	"	"	"		"	
	"	"	"		"	
	PES	PSS/PAH + PAA/PAH 8.5+2 bilayers	50 mM NaCl, pH 6/6	12.8	1.7 bar, crossflow velocity 7.2 m/s	14
	"	"	"		"	
	"	"	"		"	
	"	"	"		"	
	"	"	"		"	
	PES	PSS/PAH + PAA/PAH 7.5+3 bilayers	50 mM NaCl, pH 6/6	8.9	1.7 bar, crossflow velocity 7.2 m/s	12
	"	"	"		"	
	"	"	"		"	
	"	"	"		"	
	"	"	"		"	
	PES	PSS/PAH + PAA/PAH 6.5+4 bilayers	50 mM NaCl, pH 6/6	6.8	1.7 bar, crossflow velocity 7.2 m/s	13
	"	"	"		"	
	"	"	"		"	
	"	"	"		"	
	"	"	"		"	

Table S4.2b. Continuation of overview of micropollutant removal in literature and this study.

Author	Micropollutant	Retention (%)	pH	Equilibration (h)	Feed concentration (µg/L)	Matrix	Remarks
Fujioka et al. 2014 [29]	naproxen sulfamethoxazole	98	8	8	0.3	20 mM NaCl 1 mM NaHCO ₃ 1 mM CaCl ₂	salt retention in same matrix
		99					
		90					
		92					
	atenolol atrazine bisphenol A	50					
		92	8	8	0.3	20 mM NaCl 1 mM NaHCO ₃ 1 mM CaCl ₂	salt retention in same matrix
		92					
		58					
Xu et al. 2005 [30]	naproxen naproxen naproxen naproxen	98	6	?	0.3	some NaCl and CaCO ₃	NaCl retention according to Dow Filmtec
		99	6	?			
		98	6	?			
		27	6	?			
	naproxen	96	6	?			NaCl retention according to Koch/Lenntech
Kimura et al. 2003 [31]	bisphenol A	45	7	8	100	MilliQ	NaCl retention according to Dow Filmtec
	bisphenol A	99	7	8			
Kimura et al. 2004 [32]	bisphenol A sulfamethoxazole	83	7	24	100	MilliQ	
		70	7	24			
	bisphenol A sulfamethoxazole	18	7	24			
		82	7	24			
Yüksel et al. 2013 [33]	bisphenol A	98	7	6	50000	MilliQ	NaCl retention according to GE/Lenntech NaCl retention according to Dow Filmtec
	bisphenol A	11	7	6			
		99	7	6			
	bisphenol A	81	7	6			
	bisphenol A	98	7	6			
	bisphenol A	98	7	6			
Bolong et al. [34] 2010	bisphenol A	68	5	3	5000	DI water	noncommercial, not equilibrated
Comerton et al. 2008 [35]	sulfamethoxazole	10	7	24	1	3 mM NaCl 1 mM NaHCO ₃	NaCl retention according to Dow Filmtec
	bisphenol A	5	7	24			
	sulfamethoxazole	22	7	24			
	bisphenol A	26	7	24			

	sulfamethoxazole	96	7	24			NaCl retention according to TriSep
	bisphenol A	96	7	24			NaCl retention according to TriSep
Simon et al. 2009 [36]	sulfamethoxazole	28	6	4?	750	20 mM NaCl	salt retention in 20 mM NaCl and 1 mM CaCl ₂
	sulfamethoxazole	64	6	4?		1 mM NaHCO ₃	
	sulfamethoxazole	98	6	4?		1 mM CaCl ₂	
	sulfamethoxazole	99	6	4?			
Simon et al. [37] 2012	sulfamethoxazole	82	6.3	4?			salt retention in same matrix
Chang et al. 2012 [38]	sulfamethoxazole	55	6	24	500	10 mM NaCl	NaCl retention according to Dow Filmtec
	sulfamethoxazole	43					
Verliefde et al. 2008 [39]	atenolol	94	7	96	10000	5 mM NaCl	
	bezafibrate	98	7				
	atenolol	90	7				
	bezafibrate	98	7				
Ge et al. 2017 [40]	sulfamethoxazole	61	7	?	200	MilliQ	
	naproxen	86	7				
	bezafibrate	79	7				
Dang et al. 2014 [41]	bezafibrate	97	8	1?	100	10 mM NaCl, 1 mM NaHCO ₃	NaCl retention according to Dow Filmtec
	sulfamethoxazole	96	8			1 mM CaCl ₂	
Zhang et al. 2004 [42]	atrazine	71	7	2?	5000	DI water	
	atrazine	58	7				
	atrazine	93	7				
	atrazine	88	7				
Caus et al. 2009 [43]	atrazine	79	7	2	10	DI water	permeability including solutes
	atrazine	16	7				
	atrazine	84	7				
Azaïs et al. [44] 2016	atenolol	85	8	24	750	1 mM NaHCO ₃	NaCl retention determined at 8 bars
	atenolol	52	8				
Yangali et al. 2009 [45]	sulfamethoxazole	59	7	72	6.5-13	10 mM KCl	
	naproxen	76	7				
	atrazine	81	7				
	bisphenol A	29	7				
	sulfamethoxazole	94	7				NaCl retention according to Dow Filmtec
	naproxen	96	7				
	atrazine	95	7				
	bisphenol A	90	7				
Xie et al.	bisphenol A	77	7	6	500	20 mM NaCl, 1 mM NaHCO ₃	

2012 [46]							
This study	atenolol	97	5.8	20	3000	Demiwater	pH of PSS solution not adjusted
	atrazine	93					
	sulfamethoxazole	82					
	bezafibrate	98	5.8	20	3000	Demiwater	
	bisphenol A	86					
	naproxen	92					
	atenolol	96					
	atrazine	80					
	sulfamethoxazole	68					
	bezafibrate	90	5.8	20	3000	Demiwater	
	bisphenol A	86					
	naproxen	85					
	atenolol	98					pH of PSS solution not adjusted
	atrazine	97					
	sulfamethoxazole	94					
	bezafibrate	99	5.8	20	3000	Demiwater	
	bisphenol A	96					
	naproxen	98					
	atenolol	99					
	atrazine	97					
	sulfamethoxazole	96					
	bezafibrate	99.6	5.8	20	3000	Demiwater	
	bisphenol A	97					
	naproxen	99					
	atenolol	99					
	atrazine	97					
	sulfamethoxazole	96					
	bezafibrate	99.6	5.8	20	3000	Demiwater	
	bisphenol A	97					
	naproxen	99					

4.6.9 S9. Permselectivity of the PEM membranes and commercial membranes

To determine the permselectivity (relative transport rate) of the different membranes towards NaCl and micropollutants, the individual solute permeabilities were calculated. This is needed for a fair selectivity analysis, as the retention of solute in a membrane process is both determined by the membrane and the process conditions, whereas the solute permeability is only a function of the solute and membrane. For this we determined the mass transfer coefficient, k , by the following equation [47]:

$$k_{fs} = 1.62 \left(\frac{v D_i^2}{d_h L} \right)^{0.33} \quad (4.2)$$

with v the tangential cross velocity of the feed (ms^{-1}), D_i the diffusion coefficient of the solute in water (m^2s^{-1}), d_h the hydraulic diameter of the feed channel (m) and L the channel length (m). If no NaCl data were provided in the paper, we used the manufacturer's data available from the data sheets of the membrane. In the case of the hollow fibers experiments that were performed in the turbulent regime, we used the Linton Sherwood correlation:

$$k_{hf} = 0.023 \frac{D_i}{d_h} \left(\frac{\rho v d_h}{\eta} \right)^{0.8} \left(\frac{\eta}{\rho D_i} \right)^{0.33} \quad (4.3)$$

The diffusion coefficients of the micropollutants in water were estimated by the Hayduk and Laudie method [48]:

$$D_i = \frac{13.26 \times 10^{-9}}{\eta^{1.4} (MW)^{0.589}} \quad (4.4)$$

The ratio between the mass transfer coefficient k and the convective water transport through the membrane, J (ms^{-1}), is referred to as the concentration polarization factor. This the effective ratio of the transport of the solute to the membrane and the back transport by diffusion. In the few cases where this ratio was provided by the original authors (Yangali-Quintanilla et al. 2009 [17], Verliefde et al. 2008 [11], Xu et al. 2005 [2]), we used their values accordingly. With the concentration polarization factor the true solute concentration at the membrane surface can be determined, according to:

$$e^{\frac{J}{k}} = \frac{c_m - c_p}{c_b - c_p} \quad (4.5)$$

With c_m being the solute concentration at the membrane surface (molL^{-1}), c_p the solute concentration of the permeate (molL^{-1}) and c_b the solute concentration of the feed (molL^{-1}). The retention R (-) of a membrane process is determined via [49]:

$$R = 1 - \frac{c_p}{c_m} = \frac{J}{J + B e k} \quad (4.6)$$

Equation 6 allows us to determine the solute permeability coefficient, B (ms^{-1}), of a membrane, which is a process independent measure of the transport rate of solutes through a membrane. We then defined the permselectivity of the membranes by the ratio of the permeability coefficients of salt (B_{NaCl}) and the micropollutants ($B_{\text{micropollutant}}$).

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Chapter 5

Role of Polycation and Crosslinking in Polyelectrolyte Multilayer Membranes

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Abstract

Alternate deposition of oppositely charged polyelectrolytes is an excellent approach to control the chemistry of interfaces. Membrane technology in particular is one field that benefits from the simplicity and tunability of polyelectrolyte multilayers (PEMs). Herein, ultrafiltration support membranes are coated with PEMs in order to fabricate nanofiltration membranes. Three different PEMs, of vastly different polymeric structure, namely those of poly(4-styrene sulfonate) (PSS)/poly(allylamine hydrochloric acid) (PAH), PSS/poly(ethyleneimine) (PEI, branched), and PSS/poly(4-aminostyrene) (PAS) are prepared and studied from a fundamental perspective in terms of multilayer composition and crosslinking, and also from an applied perspective through PEM membrane performance. For the PSS/PAH multilayers, a 30–40% polycation excess and positive membrane surface charge was measured. The PSS/PEI and PSS/PAS systems have much lower polycation excesses (~10%) and negative membrane surface charges. The low molecular weight cut-off (MWCO) of the PSS/PAH membranes signifies their dense structure (high chain packing density), while ion retentions indicate that the dielectric exclusion mechanism is dominant. The PSS/PEI membranes are even denser and perform better; with the smaller excess of PEI giving a more stoichiometric and less hydrated layer. In contrast, the PSS/PAS membranes are more open, which is likely due to the lower charge density of PAS compared to PEI and PAH. After chemical crosslinking, all of the PEM membranes are denser and therefore less permeable to water, but, overall crosslinking is beneficial to membrane separation performance. For the application of micropollutant separation, retention increases for denser multilayers (PEI > PAH > PAS). After crosslinking, micropollutant retention increases for the PSS/PAH membranes, whereas little to no improvement is seen for the PSS/PAS and PSS/PEI membranes. Overall, this study shows that completely different membrane properties can be obtained by changing the type of polycation, thus demonstrating the high versatility of PEM based membranes. In addition, for all PEM membranes, crosslinking acts as an additional tuning parameter that leads to denser and more selective layers.

5.1 Introduction

Building polyelectrolyte multilayers (PEMs) is a simple and versatile approach to modify the chemistry of surfaces and thus control various interfacial phenomena. Consequently, over the last two decades, significant interest has been focused on the preparation of PEMs and in understanding their behavior. The list of parameters that can be used to tune PEMs is vast and includes salt concentration, [1] pH, [2, 3] polyelectrolyte (PE) type, [4] the number of layers, [5] crosslinking, [6] and PE molecular weight. [7] In addition, various PEM fabrication methods exist including dip-coating (the most common), spray coating, spin coating, dynamic coating, and electrodeposition. [8] Over the years, PEMs have found interest in fields such as membrane technology, [9] catalysis, [10] semiconductors, [11] drug delivery, [12] and optical devices [13] since layer thickness, affinity, and refractive indices can be controlled. Concerning the field of membranes, the layer-by-layer (LbL) dip-coating approach [14] to preparing PEMs has become widely used to coat a selective layer on the inner surface of hollow fiber support membranes. [9] In addition, PEs have been used to create microfiltration membranes with anti-viral properties, [15] to modify electrodialysis membranes to increase selectivity, [16, 17] and to prepare nanofiltration (NF) membranes [9] that are already used for commercial applications. [18]

Many PE combinations have been studied in order to fabricate PEM membranes. Coating poly(diallyldiammonium chloride) (PDADMAC) and poly(4-styrene sulfonate) (PSS) multilayers on ultrafiltration (UF) support membranes creates successful NF membranes with long term physical and chemical stability (for example towards hypochlorite, a typical membrane cleaning chemical). [19] In addition, PEM membranes based on PDADMAC and PSS show high monovalent ion selectivity toward chloride–sulfate, [20] fluoride, [21, 22] and phosphate. [23] Poly(vinylamine) in combination with poly(vinyl sulfonate) was used to obtain PEM membranes with reverse osmosis properties. [24, 25] Interestingly, for PSS/PDADMAC PEMs an excess of PDADMAC within the bulk of the multilayer [26] is found and this directly influences membrane performance by making the bulk of the multilayer positively charged. [27] Another well-studied PE pair is the combination of poly(allylamine hydrochloric acid) (PAH) with PSS. For this PE pair, a polycation, PAH in this case, is also found to be in excess within the bulk of the multilayer. [1, 28] It is interesting to note that both of these common PEM systems, PDADMAC/PSS and PAH/PSS, tend to have an excess of the polycation in the bulk of the multilayer. Such a PE excess depends on the given PE pair, and can be beneficial to separation performance. But this PE excess can also lead to swelling of the multilayer, which increases its effective pore

size (i.e. makes the layer less dense/more open). It is therefore of interest to study the performance of PEM membranes that exhibit different degrees of excess PE and thus difference swelling behavior.

The primary amine groups along PAH chains can be crosslinked in order to increase salt retentions [29, 30] and stability. [31] Crosslinking of PEMs has been achieved using glutaraldehyde (GA) and by using GA in combination with ultraviolet light (UV). [29] All studies using the PAH/PSS combination observed densification of the multilayers and increases in membrane selectivity toward ions after crosslinking, however, this came with the cost of lower permeability. In this study, PEMs are coated on the inside of hollow fiber support membranes. Coating on the inside, prevents techniques like UV light from being used for crosslinking and for this reason GA is used for crosslinking.

While, there does already exist separate literature on the buildup of different PEMs as well as the performance of different PEM-coated membranes, what is lacking is a comprehensive study that directly links multilayer buildup with PEM membrane performance. This is what we present in this work. Herein, a critical evaluation of the effect of multilayer composition and crosslinking on membrane performance depending on the type of PEM is presented. The polyanion PSS is combined with three different weakly charged polycations of varying polymeric structure; namely the linear and aliphatic PAH, the branched poly(ethyleneimine) (PEI), and the aromatic poly(4-aminostyrene) (PAS). While the PSS/PAH combination is commonly studied for PEM membranes, the combinations of PSS/PEI (using branched PEI) and PSS/PAS have not been used for preparing nanofiltration PEM membranes. The three weak polycations used all contain primary amine functional groups and thus can be readily crosslinked with GA. In addition, the PSS/PAH multilayers are built using three different salt concentrations; 5, 50, and 500 mM. All PEMs are characterized in terms of their fundamental buildup using reflectometry (PE adsorption) and zeta potential (surface charge) measurements. Subsequently, in order to obtain a deeper understanding on the relationship between PEM membrane performance and the fundamental PEM buildup, including parameters like bulk and surface charge as well as density, the PEM membranes are evaluated in terms of their ability to retain various ions and organic molecules. Finally, all PEM membranes are studied for the application of micropollutant retention.

5.2 Materials and Methods

5.2.1 Materials

Poly(allylamine hydrochloric acid) (PAH, $M_w=150,000 \text{ g}\cdot\text{mol}^{-1}$, 40 wt.% in water) was purchased from Nittobo Medical, Japan, poly(4-aminostyrene) (PAS, $M_w>150,000 \text{ g}\cdot\text{mol}^{-1}$) from Polysciences Europe GmbH, while branched poly(ethylene imine) (PEI, primary, secondary, and tertiary amine ratio: 1:1.2:0.76, $M_w=75,000 \text{ g}\cdot\text{mol}^{-1}$), and poly(sodium 4-styrenesulfonate) (PSS, $M_w=200,000 \text{ g}\cdot\text{mol}^{-1}$, 30 wt.% in water) were purchased from Sigma-Aldrich. Glutaraldehyde (25 wt.% in water) was purchased from Alfa Aesar. Sodium chloride was obtained from Akzo Nobel, magnesium chloride from Boom B.V., and magnesium sulfate and sodium sulfate from Sigma-Aldrich. Sulfamethoxazole was purchased from Fluka and atenolol, atrazine, bezafibrate, bisphenol A, bromothymol blue, naproxen, and phenolphthalein were obtained from Sigma-Aldrich. All chemicals were used without any further purification.

Tight ultrafiltration hollow fiber membranes are used as supports and were provided by NX Filtration B.V. (Enschede, The Netherlands). The fibers have a positive charge, a standard permeability of $200 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$, a standard molecular weight cut-off of 25 kDa (indicative of the pore size), and an inner diameter of 0.68 mm. The membranes are asymmetrical with the smallest pore size on the inside of the hollow fiber. Silicon wafers were obtained from WaferNet Inc. (San Jose, USA).

5.2.2 Reflectometry

Polyelectrolyte multilayer (PEM) growth was quantitatively measured using optical fixed angle reflectometry, which allows an in-situ and quantitative measurement of the adsorbed amount of polyelectrolytes on top of a silicon wafer. Polyelectrolyte solutions are alternately applied in a flow cell containing a silicon wafer with an optical spacer of 82 nm thick silicon oxide layer. [32] Adsorption is measured at the stagnation point where the hydrodynamics at this point are well-defined and the mass transfer is diffusion limited. PEMs are prepared by first flowing through a solution containing PAH, PEI, or PAS (the polycation) with the desired salt concentration. Subsequently, the wafer is rinsed with a solution of the same ionic strength, but without any polyelectrolyte, until a stable adsorption plateau is reached. After rinsing, a solution containing PSS (polyanion) with the same salt concentration is passed through the cell. After the polyanion coating step, the wafer is rinsed in the same manner as after the polycation coating step. This cycle finishes one bilayer and is repeated until 11 bilayers (22 layers) are constructed on the

silicon wafer. All polyelectrolyte solutions contain 0.1 g·L⁻¹ of the given polyelectrolyte. For the PSS/PAH multilayers, salt concentrations of 5, 50, and 500 mM NaCl were used. For the PSS/PEI and PSS/PAS multilayers, 50 mM of NaCl was used. The salt concentration of all polyelectrolyte and rinsing solutions was kept the same during multilayer growth/buildup. The polycation solutions were adjusted to have a pH of 2, while the pH of the PSS and rinsing solutions was 5.5 and 5.5, respectively.

Optical fixed angle reflectometry uses monochromatic light of a He-Ne laser (632.8 nm) which is linearly polarized and reflected from the silicon wafer at the Brewster angle (71°). The polarized light is subsequently split into its parallel and perpendicular component and both component intensities are measured in the detector. The signal (S) is defined as the fraction of the parallel over the perpendicular components. The difference between the signal (ΔS) and the signal at the initial state (S_0) over the initial state signal is proportional to the adsorbed amount on the silicon wafer, as shown in **Equation 5.1**.

$$\Gamma_i = Q_i \cdot \frac{\Delta S}{S_0} \quad (5.1)$$

In **Equation 1**, Γ is the adsorbed mass (mg·m⁻²) and Q the sensitivity factor (mg·m⁻²). The sensitivity factor or Q -factor depends on the refractive indices (n) of the used materials, thicknesses (d) of the PEM and silicon oxide layer, angle of incidence of the laser light, and the refractive index increment (dn/dc) for the PEs. The refractive index increments (dn/dc) were determined using a Schmidt+Haensch ATR-lambda refractometer at wavelengths of 590 and 700 nm. To determine the refractive index increment, the refractive index was measured at five different PE concentrations, the results are plotted in **Figure S5.1** in the supporting information. For each PE, the background salt and pH were the same as the coating solutions; PAH (pH=2 and 5, 50, or 500 mM NaCl), PEI (pH=2 and 50 mM NaCl), PAS (pH=2 and 50 mM NaCl), and PSS (pH=5.5 and 5, 50, or 500 mM NaCl). The refractive index increments and the various sensitivity/ Q -factors (by an optical model using a silicon wafer with an 82 nm silicon oxide layer) are given in **Table 5.1** for each polyelectrolyte.

Table 5.1: Refractive index increment values and the accompanying Q-factor used for calculating the adsorption of polyelectrolytes in this study by means of reflectometry.

Polyelectrolyte	Refractive index increment	Sensitivity (Q) factor
	dn/dc (mL·g ⁻¹)	(mg·m ⁻²)
PSS (-)	0.252	18.9
PAH (+)	0.227	20.9
PEI (+)	0.319	14.9
PAS (+)	0.295	16.1

The excess amount of monomers ($\Sigma_{monomer}$, mmol·m⁻²) [1] is defined as the total monomeric amount of adsorbed polycation (Γ_{PC}) minus the total monomeric amount of adsorbed PSS (Γ_{PSS}) at a given layer number of polycation (i) and polyanion (j) according to **Equation 5.2**:

$$\Sigma_{monomer} = \sum_i \Gamma_{PC} - \sum_j \Gamma_{PSS} \quad (5.2)$$

Here, the assumption is that there is no removal of any of the previously adsorbed polyelectrolytes. To obtain an excess monomer ratio, **Equation 5.3** is used:

$$Excess\ monomer\ ratio = \frac{\sum_i \Gamma_{PC} - \sum_j \Gamma_{PSS}}{\Gamma_{total}} \quad (5.3)$$

where the excess monomer (from **Equation 5.2**) is divided by the total monomeric adsorption (Γ_{total}) at a given layer number (i+j).

5.2.3 Polyelectrolyte multilayer fabrication

Tight hollow fiber ultrafiltration membranes were coated in a bundle containing 20 fibers using a dip-coat robot made from LEGO® Mindstorms in cylinders containing the desired solutions. The positively charged support membranes were first immersed in a solution containing 0.1 g·L⁻¹ polyanion and the appropriate ionic strength for 15 minutes. Subsequently, the membranes were rinsed in three separate cylinders containing the same ionic strength as the coating solutions for 5 minutes per rinsing step. Finally, the membranes were immersed in a solution containing 0.1 g·L⁻¹ polycation and the desired ionic strength. This cycle completes one bilayer and is repeated until ten bilayers are coated, each PEM is terminated by the polycation.

Three different salt concentrations of 5, 50, and 500 mM NaCl were used to fabricate three different [PSS/PAH]₁₀ PEMs (the notation used here corresponds to a final PEM made up

of 10 bilayers of PSS and PAH). For fabrication of the [PSS/PEI]₁₀ and [PSS/PAS]₁₀ PEMs, a salt concentration of 50 mM NaCl was used. The pH values for the polyanion (PSS), the polycation (PAH, PEI, and PAS) and the rinsing solutions were 5.5, 5.5, and 2, respectively.

Crosslinking was performed in an aqueous solution of demineralized water containing 0.1 wt.% of glutaraldehyde at a pH of 5.5 in a volumetric cylinder. Crosslinking a primary amine with GA is called a Schiff-base reaction at which an imine bond is formed. [6] After preparing the hollow fiber PEM membranes, they were immersed in the crosslinking solution in the same manner as the dip-coating steps for 16 hours. After crosslinking, the PEM membranes were rinsed in demineralized water for at least 2 hours. Before drying, the membranes were immersed for at least 4 hours in an aqueous solution containing 15 wt.% of glycerol to prevent pore collapse of the UF support membranes. After being dried, the hollow fibers were potted into modules with an approximate active fiber length of around 17 cm. For each PEM membrane, five separate single fiber modules were prepared and studied.

5.2.4 Zeta potential

For the zeta potential measurements, prepared PEM hollow fiber membranes were fixed with glue in polyethylene tubes in such a way that the membranes were unable to permeate from the lumen to shell side (inside to out) but there can remain crossflow through the lumen side (inside) of the hollow fiber membrane. For the measurements, three different modules were fabricated and measured. Zeta potential was measured by an electrokinetic analyzer (SurPass, Anton Paar, Graz Austria) by flowing a 5 mM KCl solution under a given pressure difference through the hollow fiber module. The flow through the module at a defined pressure difference (Δp , Pa) creates a streaming current (dI , A) from which the zeta potential (ζ , V) can be calculated using **Equation 5.4**;

$$\zeta = \frac{dI}{dp} \cdot \frac{\eta}{\epsilon \cdot \epsilon_0} \cdot \kappa_B \cdot R \quad (5.4)$$

Where η is the solution viscosity in Pa·s, ϵ the dielectric constant of the electrolyte (-), ϵ_0 the dielectric constant of vacuum (-), the specific conductivity of the solution is defined as κ_B (S·m⁻¹), and R (Ω) is the measured Ohmic resistance of the hollow fiber module.

5.2.5 Membrane performance measurements

The performance of the PEM hollow fiber membranes was determined by measuring permeability, salt retention, molecular weight cut-off, and micropollutant retention. All measurements applying a hydraulic pressure were performed on a crossflow setup. This

setup has a rotary vane pump (BN71B4 pump motor, Bonfiglioli, Italy; IMTI 1.5M inverter, Electroil, Italy; PA411 pump head, Fluid-o-Tech, Italy).

5.2.6 Permeability

Membrane permeability towards water was measured with Milli-Q (18.2 M Ω) water at an applied transmembrane pressure of 6.2 bars using the setup described above. The time is measured using a stopwatch and at least 10 mL is collected before measuring the permeate weight. Using the time, permeate weight, and the applied transmembrane pressure the permeability can be calculated as in **Equation 5.5**;

$$\text{Permeability} = \frac{m_p}{\rho_w \cdot A_i \cdot t \cdot P_{tmp}} \quad (5.5)$$

Here, m_p is the mass of the collected permeate in g, ρ_w is the density of water in g·L⁻¹, A_i the inner membrane surface area in m⁻², t the time in hours, and P_{tmp} the transmembrane pressure in bar.

5.2.7 Salt retention

Retentions of NaCl, Na₂SO₄, MgCl₂, and MgSO₄ were determined separately at a concentration of 5 mM in demineralized water. These measurements were performed on the same setup as described above, under crossflow condition at an applied pressure of 6.2 bars and at a crossflow velocity of 1 m·s⁻¹. This crossflow velocity corresponds to a Reynolds number of 675, well within the laminar flow regime. The retention R was determined by measuring the conductivity of both the permeate and feed using the relationship presented in **Equation 5.6**;

$$R = \frac{\Delta C}{C_{\text{feed}}} \cdot 100\% \quad (5.6)$$

where, ΔC and C_{feed} correspond to the difference between the feed and permeate concentration and the feed concentration, respectively.

5.2.8 Molecular weight cut-off

Using a feed mixture of ethylene glycol (EG), diethylene glycol (DEG), and several molecular weights of poly(ethylene glycol) (PEG) molecules; EG62, DEG106, PEG200, PEG400, PEG600, PEG1000, PEG1500 and PEG2000 at a concentration of 1 g·L⁻¹ each the molecular weight cut-off of the membranes was determined. The measurement was performed in crossflow and operated at 2 bar and a crossflow velocity of 1 m·s⁻¹ per module containing one hollow fiber. Both permeate and feed samples were taken and

analyzed via Gel Permeation Chromatography with a size exclusion column (SEC) (Agilent 1200/1260 Infinity GPC/SEC series, Polymer Standards Service data center and column compartment). Solution were flown over two Polymer Standards Service Suprema 8x300 mm columns in series: 1000 Å, 10 µm followed by 30 Å, 10 µm at 1 mL·min⁻¹ and concentrations were measured via refractive index measurements.

5.2.9 Micropollutant retention

The retention of micropollutants was measured using a cocktail containing atenolol, atrazine, bezafibrate, bisphenol A, bromothymol blue, naproxen, phenolphthalein, and sulfamethoxazole. Of each micropollutant, 3 mg·L⁻¹ was dissolved and the pH of the solution was adjusted to 5.8. Using a crossflow setup, retention was measured at a pressure of 6.2 bar and 1 m·s⁻¹ crossflow velocity per module. Prior to measuring permeate samples, the filtration was allowed to stabilize for at least 16 hours in order to remove the influence of adsorption on the reported retention values. [33] A calibration range was prepared from the feed and from each module around 2 mL of permeate was collected. Analysis of all samples was performed by HPLC (High pressure liquid chromatography, Dionex Ultimate 3000, Eluent: water, acetonitrile, and 0.1% phosphoric acid) over a Thermo Scientific Acclaim RSLC 120 C18 column (2.2 µm, 2.1x100 mm). Here, the column oven temperature was 40°C and the flow rate of the mobile phase was 0.8 mL·min⁻¹. The used eluent starts with 5% water and linearly increases until it contains 90% water, acetonitrile, and 0.1% phosphoric acid. The micropollutant concentrations were determined via UV/Vis detection at 225 nm, and bromothymol blue at 430 nm. Subsequently, micropollutant retention was calculated using equation 6.

5.3 Results and Discussion

In this section, the results will be presented and discussed in two distinct parts. First, the fundamental buildup of the polyelectrolyte multilayers (PEMs) and the zeta potential of the final multilayers will be discussed. Next, the PEM-coated hollow fiber membranes and their nanofiltration properties are studied in three subsections: the effect of multilayer composition on membrane performance, the effect of crosslinking on membrane performance, and the application of the PEM membranes for micropollutant removal.

Figure 5.1: Chemical structures, full names, abbreviation, charge, and molecular weight of the polyelectrolyte monomers used. Monomers are shown in their charged form.

5.3.1 Multilayer characterization

Optical fixed angle reflectometry is a tool to quantitatively study the buildup of PEMs. [9] In this study, the effect of polycation type on the preparation of PSS based multilayers is studied. The three polycations used are PAH, branched PEI, and PAS (chemical structures and monomer molecular weights are shown in **Figure 5.1**). From these PEMs, PSS/PAH is well known, using branched PEI for PEM membranes has only been performed on ion-exchange membrane, [34] whereas PAS is a polycation that is known to built multilayers [35] but new to the PEM membrane literature. The PSS/PAH multilayers were prepared at three different NaCl concentrations of 5, 50, and 500 mM, whereas the buildup of the PSS/PEI and the PSS/PAS multilayers is studied at 50 mM NaCl. First focusing on the PSS/PAH systems shown in **Figure 5.2A**, it is seen that the adsorbed molar amount of

the polyelectrolytes increases when higher salt concentrations are used, which is in line with typical PEM behavior at higher ionic strengths. [9] At low salt concentration, the charge of the polyelectrolytes within the multilayer will be intrinsically compensated by the opposite polyelectrolyte. [36] When salt concentration increases, the salt screens the electrostatic interactions of the polyelectrolytes, thus making the polyelectrolytes extrinsically compensated. [36-38] The intrinsic and extrinsic charge compensation is seen back in the reflectometry results, where at 5 mM, the buildup of the PSS/PAH multilayer is linear. For 50 and 500 mM, initially, in the first few layers the PSS/PAH systems grow non-linearly. After these initial layers, the buildup is linear and the buildup is larger at higher salt concentration; similar to what is reported in other studies due to more extrinsic charge compensation. [1] When the polycation is changed to PEI, it is observed that the molar adsorption is lower than that of PSS/PAH multilayers built at the same salt concentration. With PAS as a polycation, the adsorption is even lower and closer to the PSS/PAH multilayer constructed at 5 mM of NaCl. The adsorption of both PEI and PAS is lower and is most likely due to the differences in polyelectrolyte structure compared to PAH. Here, PEI has a branched structure and PAS has a bulky aromatic structure meaning that both these polycations will have a decreased mobility and therefore can penetrate less in the multilayer, resulting in a lower adsorption for PEI and PAS.

In **Figure 5.2B**, the amount of excess monomer in the multilayer as function of the number of layers is given (according to **Equation 5.2**). Here, a positive value corresponds to an excess of polycation within the multilayer. In **Figure 5.2B** it is observed that for the PSS/PAH based multilayers, the amount of excess polycation increases when higher salt concentrations are used during multilayer preparation. This is simply because of the increased adsorption at higher salt concentrations. An improved measure is therefore the excess monomer ratio (**Figure 5.2C**), which gives the monomer excess normalized by the layer adsorbed amount. This normalized monomer excess is constant for all three ionic strengths; meaning that the excess amount of PAH with respect to PSS is independent of the salt concentration used during layer preparation.

Figure 5.2: A: Molar adsorption as function of layer number for PSS/PAH PEMs (5, 50, and 500 mM), PSS/PEI PEM (50 mM), PSS/PAS PEM (50 mM). B: Excess monomer determined by calculating the amount of excess monomers accumulating per adsorption step. C: Excess monomers of the PEMs divided by the total molar adsorption. For both B and C, a positive value corresponds to an excess amount of polycations within the multilayer. Error bars are standard errors of measurement on three separate samples.

For the PSS/PEI and the PSS/PAS multilayers built at 50 mM NaCl, a different trend is seen where now the amount of excess polycation accumulating within the multilayer is significantly lower than the PSS/PAH multilayers. When looking at the excess monomer ratio of Figure 2C, which is the monomer excess normalized for the molar adsorption as calculated by equation 3, it is observed that for the PSS/PAH multilayers monomer excess level offs at around 30–40% of excess PAH (with respect to PSS), in line with other studies.[1, 28] For the PSS/PEI multilayers, in the first few layers PEI is 10–40% in excess with respect to PSS, and this gradually decreases to 5–11% as the number of layers increases. The PSS/PAS multilayer is similar to the PSS/PEI multilayers, with the amount of excess polycation with respect to PSS stabilizing at higher layer numbers, at a charge ratio for PAS of 10–16%. Again, this lower polycation excess for the PEI and PAS multilayers compared to PAH multilayer can be related to the steric differences in polycation structure; branched and aromatic side groups vs linear and small side groups. It is important to note that the three polycations used are all weakly charged. Their ionizable nature means that they do not need to be completely charged during multilayer formation (i.e. during adsorption) and this can lead to polycation excesses since the strong polyanion PSS is always fully charged. In the literature it is common for PSS/PAH [1, 28] multilayers to have an excess of PAH. For PSS/PEI and PSS/PAS multilayers there is no literature on monomer/charge excess. For PSS/PAH multilayers, the excess of PAH is attributed to the high charge density of PAH, as the PAH monomer is quite small. In this case, the Bjerrum length is larger than the average distance of the PAH charges and as a consequence, Manning condensation occurs and this immobilizes counterions on the charges of PAH and therefore an excess of PAH can accumulate within the layer. [1] This excess amount of polycation can lead to more extrinsic charge compensation and thus more swelling than for an intrinsically charge compensated multilayer. [39] The results presented in Figure 2, show that an excess amount of polycation is also present in PSS/PEI and PSS/PAS multilayers. However, this excess is much lower than in PSS/PAH multilayers and could be due to a better match between the polycation and polyanion since PAS and PSS have similar chemical structures and the branched structure of PEI makes it more flexible to compensate charges.

Table 5.2 presents the measured zeta potential of the uncoated and PEM coated hollow fiber membranes, the PEMs have ten bilayers and all PEMs are terminated with the polycation. The zeta potential measurements reveal the charge of the final surface and show that the uncoated support membrane has a positive surface charge. All the [PSS/PAH]₁₀ multilayer membranes have a positive surface charge, while both the

[PSS/PEI]₁₀ and [PSS/PAS]₁₀ multilayers have negative surface charge, even though the polycation is the terminating layer. The measured negative surface charge for the PEI and PAS membranes is somewhat surprising, however, the polycations are weak PEs and as discussed above they do not need be fully charged during buildup or within the resultant multilayer, whereas PSS is a strong PE and is therefore always fully charged. This means that although an excess of polycation is measured within the multilayers (Figure 2C), it is still possible for them have a negatively charged surface. Moreover, the excess of PEI and PAS (5–16%) is much lower than that of PAH (30–40%). Crosslinking shows little to no influence on the measured zeta potential and overall, it can be concluded that crosslinking does not significantly influence the surface charge of the PEMs.

Table 5.2: Zeta potential of the support membrane and the PEM membranes non-crosslinked and crosslinked. Error bars are standard deviations of measurements on three different membrane modules.

	Zeta potential (mV) Non-crosslinked	Zeta potential (mV) Crosslinked
Support membrane	29 ± 9	N.A.
5 mM – [PSS/PAH] ₁₀	11 ± 2	1 ± 2
50 mM – [PSS/PAH] ₁₀	18 ± 6	10 ± 2
500 mM – [PSS/PAH] ₁₀	16 ± 3	17 ± 2
50 mM – [PSS/PEI] ₁₀	–26 ± 9	–27 ± 2
50 mM – [PSS/PAS] ₁₀	–14 ± 4	–13 ± 1

In summary for this section, the adsorption behavior and zeta potential of PSS/PAH, PSS/PEI, and PSS/PAS multilayers were studied. For all the PSS/PAH multilayers an excess monomer ratio of PAH of 30–40%, whereas for the PSS/PEI and the PSS/PAS multilayers a much lower excess monomer ratio of polycation was found; 5–11% and 10–16% respectively. The zeta potential of the multilayers showed that the PSS/PAH membranes have a positive surface charge, however, the PSS/PEI and the PSS/PAS multilayers have a negative surface charge even though the multilayers are terminated by the polycation. In the next section, membrane performance is measured using ions and

various molecules and from this, more information about the bulk layer properties of the PEMs as well as the effect of crosslinking will be attained.

5.3.2 Nanofiltration results

In this section, the nanofiltration performances of the different PEM systems are presented and discussed. As before, five different PEM membranes have been studied; [PSS/PAH]₁₀ multilayers prepared at 5, 50, and 500 mM NaCl, as well as a [PSS/PEI]₁₀ and a [PSS/PAS]₁₀ multilayer both prepared at 50 mM NaCl. The section is split up in three parts: the effect of polycation and multilayer composition on membrane performance; the effect of crosslinking on multilayer composition and membrane performance; and the application of the fabricated PEM membranes for micropollutant removal.

5.3.2.1 Effect of polycation

In order to obtain more knowledge about the packing density, amount of chains per volume, of the different PEM membranes, permeability and molecular weight cut-off (MWCO) experiments have been performed with the results shown in **Figure 5.3**. Permeability gives information about how easily water passes through the PEM, e.g., high permeability means low resistance for water to permeate through the layer. Subsequently, when the PEM is denser, permeability will be lower due to densely packed PE chains, and therefore, the effective pore size will be small due to a high interchain network density. However, a simple increase in thickness also leads to lower permeability although the density of the PEM will stay the same. Here, MWCO experiments give additional knowledge about the density of the multilayer. In this experiment, neutral PEG molecules of various sizes are retained by the PEM membranes, which is again an indication of the packing density of the PE chains within the multilayer, one that does not depend on layer thickness. In **Figure 5.3A**, the permeability (left axis) and MWCO (right axis) of [PSS/PAH]₁₀ PEM membranes are plotted as function of the salt concentration used during preparation. When a [PSS/PAH]₁₀ PEM is fabricated at 5 mM, the PEM membrane has a water permeability of $22 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ and the permeability decreases to 9 and $6 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ when the ionic strength used during preparation is increased to 50 and 500 mM, respectively. The permeability decreases at higher salt concentrations due to the higher adsorbed amount of the polyelectrolytes and thus thicker layers are formed, as shown by the reflectometry results in **Figure 5.2A**. These results are similar to studies performed on PSS/PDADMAC PEM membranes where the permeability is also highly dependent on the salt concentration used during preparation. [9] In the same Figure, the

MWCO is plotted and it is observed that at 5 mM the MWCO is very high, which indicates that this layer has pinhole defects because the pores of the support are not fully covered. The MWCO for the PEMs prepared at 50 and 500 mM is much lower and similar to each other. At these higher salt concentrations the multilayers are thicker, and therefore, the pores are fully covered and a defect-free multilayer is formed with a low MWCO. [9]

In **Figure 5.3B**, the water permeability (left axis) and MWCO (right axis) is plotted for the [PSS/PAS]₁₀, the [PSS/PAH]₁₀, and the [PSS/PEI]₁₀ PEM membranes that were prepared at the same salt concentration of 50 mM NaCl. It is known that by increasing the charge density (number of ion pairs per number of carbon atoms) of a PEM results in higher retentions toward ions. [40] In this study, PSS/PAH, PSS/PEI, and PSS/PAS have respectively an ion pair per number of carbon atoms of 1/11, 1/10, and 1/16. Here, PSS/PAH and PSS/PEI are close together and have high charge densities and PSS/PAS has a low number of ion pairs per number of carbon atoms, and therefore, a low charge density. When the various PEMs are tested, it is observed that by switching the chemistry by using another polycation, large differences in permeability and MWCO are found. When comparing [PSS/PAH]₁₀ to [PSS/PEI]₁₀, the permeability decreases from 9 to 4 L·m⁻²·h⁻¹·bar⁻¹ and the MWCO decreases from 267 to 239 g·mol⁻¹. This is a 56% change in permeability, which is noticeably lower than any of the PSS/PAH PEM membranes used in this study. This is surprising as the PEI/PSS layer is expected to be thinner (Figure 2A) than the PAH/PSS layer. Together with the observed lower MWCO, this indicates that the PEM is significantly denser when the polycation is changed from PAH to PEI. However, the PSS/PEI multilayer is much denser than expected since the polyelectrolyte charge densities of both PSS/PAH and PSS/PEI are similar. The increased density of the PSS/PEI multilayer can be explained by the much lower excess of polycation present, which helps creates a more stoichiometric multilayer. A more stoichiometric multilayer will result in less swelling of the layer swelling (as the charge is lower), better ion pairing, [41] and therefore, will result in a higher packing density of PE chains. On the contrary, when PAS is used as a polycation, the polyelectrolyte charge density is lower than for PSS/PAH and PSS/PEI and this results in a high permeability for the [PSS/PAS]₁₀ membrane of 22 L·m⁻²·h⁻¹·bar⁻¹, an increase of 144% with respect to the PSS/PAH multilayer membrane built at the same salt concentration. The MWCO of the PEM membranes matches this change in water permeability. Here, the MWCO increases from 267 g·mol⁻¹ for the PSS/PAH membrane to 713 g·mol⁻¹ for the PSS/PAS membrane, indicating a more open PEM when PAS is used as the polycation. Importantly though, the MWCO measured for the PSS/PAS membranes is still well within the nanofiltration regime and the higher

MWCO is in line with the higher water permeability observed. Moreover, even though the PSS/PAS multilayer constructed with 50 mM of salt has similar PE adsorption behavior as a 5 mM PSS/PAH multilayer (see Figure 2), for the PAS case a defect-free multilayer can be prepared unlike for the 5 mM PSS/PAH case.

Figure 5.3: A: Permeability (left) and MWCO (right) of $[\text{PSS}/\text{PAS}]_{10}$, $[\text{PSS}/\text{PAH}]_{10}$, and $[\text{PSS}/\text{PEI}]_{10}$ PEM membranes prepared at a fixed salt concentration of 50 mM NaCl. B: Permeability (left) and MWCO (right) of $[\text{PSS}/\text{PAH}]_{10}$ prepared at a salt concentration of 5, 50, and 500 mM NaCl. MWCO is measured at a crossflow velocity of $1 \text{ m}\cdot\text{s}^{-1}$, pressure of 2 bar, and a temperature of 20°C . Error bars are standard errors from measurement of five separate membrane modules.

When looking at the retention values toward NaCl that are presented in **Figure 5.4A**, for the $[\text{PSS}/\text{PAH}]_{10}$ PEM membranes the retention increases with increasing salt concentration used during buildup. This is a result of increasing positive charge within the multilayer when the salt concentration increases. However, like shown in Figure 2C, the amount of excess PAH in a PSS/PAH multilayer with regard to PSS is fixed and independent of the salt concentration. For this reason, the increasing positive charge, and therefore, NaCl retention is most likely due to an increasing amount of extrinsic charge within the multilayer due to the high salt concentration used during buildup. The $[\text{PSS}/\text{PEI}]_{10}$ PEM membrane has the lowest water permeability and MWCO of all PEMs (Figure 3A) and it is also the membrane with the highest retention toward NaCl, when

compared to the other PEMs build at the same salt concentration (**Figure 5.4B**). This is again in line with the dense packing of the PE chains which translates into high dielectric exclusion, and therefore, high ion retentions. Conversely, the [PSS/PAS]₁₀ PEM membrane with the most open structure has naturally the highest water permeability and also the lowest NaCl retention, due to a low packing and charge density of PE chains. These results show that both the packing density of polyelectrolyte chains (low or high permeability), the charge density, and excess amount of monomers of the multilayer greatly influences the retention toward salt ions.

Measuring MgSO₄ retention gives useful information since two divalent ions have to be retained by the membrane instead of monovalent Na⁺ and Cl⁻ ions. In most cases, retentions for MgSO₄ are higher than for NaCl. In **Figure 5.4A**, it is observed that MgSO₄ retentions are high for each PSS/PAH PEM membranes, except the defect containing [PSS/PAH]₁₀ multilayer constructed at 5 mM NaCl. Moreover, a small decrease in MgSO₄ retention is observed when the multilayer is prepared at 500 mM instead of 50 mM. As explained in the previous paragraph, this could be due to the increased amount of extrinsic charge within the bulk of the multilayer due to the higher salt concentration used during buildup. For this reason, a higher positive charge within the bulk of the multilayer can create a higher sulfate affinity meaning that less MgSO₄ will be retained. In **Figure 5.4B**, the MgSO₄ retention of PSS/PAS and PSS/PEI membranes are compared to PSS/PAH prepared at the same salt concentration of 50 mM. Here, it is shown that PSS/PAS membranes have a good MgSO₄ retention and the PSS/PEI membranes have a very high retention of MgSO₄. The high retention of PSS/PEI PEM membranes is most likely due to a combined effect of surface/bulk charge, dielectric, and size exclusion because of the densely packed multilayer.

Figure 5.4: A: Retention of various ions (NaCl, MgSO₄, Na₂SO₄, and MgCl₂) with [PSS/PAH]₁₀ PEM membranes prepared at 5, 50, and 500 mM NaCl. Retention is measured at a crossflow velocity of 1 m·s⁻¹, pressure of 6.2 bar, and a temperature of 20°C. B: Retention of the same ions with [PSS/PAS]₁₀, [PSS/PAH]₁₀, and [PSS/PEI]₁₀ PEM membranes prepared at a fixed salt concentration of 50 mM NaCl. Error bars are standard errors from measurements on five separate membrane modules.

Focusing on the MgCl₂ retentions presented in **Figure 5.4A**, it is clear that the retention of MgCl₂ is high (>95%) for the [PSS/PAH]₁₀ multilayers constructed at 50 and 500 mM, in line with the reflectometry and zeta potential results that reveal a positive bulk and surface charge. The low MgCl₂ retention for the PSS/PAH membrane constructed at 5 mM is due to pinhole defects. However in comparison, the [PSS/PEI]₁₀ multilayer membranes shown in **Figure 5.4B** have a lower retention for MgCl₂ than the PSS/PAH membranes (50 and 500 mM), indicating a less positively charged surface and bulk. A similar behavior is observed for the more open [PSS/PAS]₁₀ membranes, where the MgCl₂ retention is even lower. For both the PSS/PEI and the PSS/PAS membranes this is completely in line with the zeta potential results which show a negative membrane surface potential. For Na₂SO₄ retention, in general for the PSS/PAH membranes a lower retention is measured than for MgCl₂. For the [PSS/PAH]₁₀ multilayer membranes the retention toward Na₂SO₄ is lower for the PEM membrane constructed at 500 mM of salt compared to the PEM membrane constructed at 50 mM. This behavior is most probably due to a greater amount of extrinsic charge present within the multilayer, and therefore, an effective higher positive charge.

For both the PSS/PEI and the PSS/PAS membranes, the very high retentions toward Na_2SO_4 are in line with the negative surface charge of the membranes (see zeta potential results).

All information from the previous sections is qualitatively summarized in **Table 5.3**, where it is shown by water permeability, MWCO, and retention of various ions that the PSS/PAH PEM membranes are overall positive charged in the bulk and surface, dense, and have a high dielectric exclusion toward ions since overall high retention toward all ions are obtained. The PSS/PAS membranes, on the other hand, are negatively charged, have an open structure, and ion retentions are low and Donnan exclusion based, since sulfate retentions are high and magnesium retentions very low. The PSS/PEI membranes are negatively charged, the densest of the PEM membranes studied in this work with the lowest permeability and MWCO, and have a high dielectric ion exclusion. In addition, the trend is seen that when the charge density of a PEM increases, the packing density of the PEM becomes higher.

Table 5.3: Summary of the PEM properties based on their nanofiltration performances for $[\text{PSS}/\text{PAS}]_{10}$, $[\text{PSS}/\text{PAH}]_{10}$, and $[\text{PSS}/\text{PEI}]_{10}$ PEM membranes prepared at 50 mM of NaCl.

PSS/PAS	PSS/PAH	PSS/PEI
Low charge density	High charge density	High charge density
1/16 ion pair per carbon atoms	1/11 ion pair per carbon atoms	1/10 ion pair per carbon atoms
Low packing density of PE chains	High packing density of PE chains	High packing density of PE chains
Negative surface charge	Positive surface charge	Negative surface charge
Low excess of polycation/low swelling potential	High excess of polycation/high swelling potential	Low excess of polycation/low swelling potential
High permeability	Medium permeability	Low permeability
Low overall ion retention	High overall ion retention	High overall ion retention
Donnan exclusion	Dielectric exclusion	Dielectric exclusion

5.3.2.2 Effect of crosslinking

In **Figure 5.5**, the MWCO is plotted as function of the membrane permeability, here, it can be clearly seen that when the permeability goes down, the MWCO decreases following the permeability-selectivity trade-off. [42] During crosslinking, the chemistry for all PEMs is the same, the primary amines react with GA forming an imine bond. [6] Subsequently, for all the PEM membranes studied the effect of crosslinking is similar; i.e. after crosslinking all the membranes have a lower water permeability and lower MWCO.

Figure 1.5: MWCO as function of the permeability for [PSS/PAH]₁₀, [PSS/PAS]₁₀, and [PSS/PEI]₁₀ PEM membranes. Solid symbols are non-crosslinked PEMs and open symbols are crosslinked PEMs. Note: CL stands for crosslinked. Black symbols are [PSS/PAH]₁₀ PEMs prepared at 5 mM (squares), 50 mM (diamonds), and 500 mM NaCl (circles). Red triangle symbols are [PSS/PAS]₁₀ PEMs and blue rectangles are [PSS/PEI]₁₀ PEMs. MWCO is measured at a crossflow velocity of 1 m·s⁻¹, pressure of 2.0 bar, and a temperature of 20°C. Error bars are standard errors from measurements on five separate membrane modules.

In **Figure 5.6**, all the ion retentions for the non-crosslinked and the crosslinked PEM membranes are plotted as function of their water permeabilities. For all the [PSS/PAH]₁₀ membranes, (black symbols) crosslinking results in lower retentions toward NaCl. This is surprising as the MWCO results shown in Figure 5 suggest that the PEMs become denser after crosslinking. A possible explanation for the decrease in NaCl retention is that the charge balance within the bulk of the multilayer changes due to the reaction of

glutaraldehyde with PAH. [6] The effect of crosslinking on NaCl retention is most significant for PSS/PAH multilayers constructed at 500 mM. When looking at the [PSS/PEI]₁₀ membranes (blue symbols), an increase in NaCl retention from 85% to 89% is observed after crosslinking. Similarly, the [PSS/PAS]₁₀ membranes (red symbols) also show an increasing retention toward NaCl after crosslinking. Here, the increases in NaCl retentions are in line with the MWCO results of Figure 5 and these data both support the conclusion that the PEMs become denser (increased chain packing density).

In **Figure 5.6B**, it is shown that after crosslinking, the retention toward MgSO₄ is not affected for any of the PEM membranes (only the water permeability is influenced). Here, either a densification and/or altering of the surface charge after crosslinking means that the MgSO₄ retention remains high. For MgCl₂ and Na₂SO₄, shown in **Figure 5.6C and D** respectively, for all PSS/PAH membranes, crosslinking leads to lower retentions toward MgCl₂ and increased retentions toward Na₂SO₄. This indicates that the overall charge of the multilayer becomes less positive. This is logical because GA reacts with the primary amine groups of PAH forming an imine, therefore, the total amount of charge is effectively decreased after reaction with GA. For both the PSS/PEI and the PSS/PAS membranes, the opposite is observed where upon crosslinking the MgCl₂ retention goes up while maintaining the same Na₂SO₄ retention. For PEI based membranes only the primary amines react, therefore, only one third of the amines present can react with GA. It could be due to an increase in packing density that the charge density increases since the secondary and tertiary amines are pulled more closely together. This is in line with a previous study on PEI based membranes where after crosslinking with terephthalaldehyde, the charge of the membranes becomes less negative. [15] For PSS/PAS, an increase in density can lead to a higher charge density within the multilayer ensuring an overall higher ion retention.

Overall, the effect of crosslinking on membrane structure and performance is the same for all PEMs (denser structure, lower overall charge and lower MWCO), but the degree to which depends on the multilayer composition, i.e. the polycation used. Here, PSS/PAH undergoes the largest changes upon crosslinking clearly showing a change in charge balance within the multilayer where the PEM becomes less positively charged within the bulk. Whereas, PSS/PEI and PSS/PAS show an overall increase in ion retention upon crosslinking due to an increasing packing density of the PE chains.

Figure 5.6: Retention of 5 mM of NaCl (A), MgSO_4 (B), MgCl_2 (C), and Na_2SO_4 (D) as function of the permeability. Solid symbols are non-crosslinked PEM membranes and open symbols are crosslinked PEM membranes. Note: CL stands for crosslinked. Black symbols are PSS/PAH membranes at which squares are the membranes buildup at 5 mM, diamonds 50 mM, and circles 500 mM NaCl. Blue rectangle symbols are PSS/PEI membranes and red triangle symbols are PSS/PAS membranes, both buildup at 50 mM NaCl. Retention is measured at a crossflow velocity of $1 \text{ m}\cdot\text{s}^{-1}$, pressure of 6.2 bar, and a temperature of 20°C . Error bars are standard errors from measurements on five separate membrane modules. Colored regions are a guide for the eye.

5.3.2.3 PEM membranes for micropollutant separation

To evaluate the performance of all the PEM membranes used in this study, difficult removable molecules that are harmful for humans and the environment (micropollutants) are treated by the fabricated PEM membranes. In **Figure 5.7A and B**, the micropollutant retentions are given for all PEM membranes used in this study. The mixture used contains various micropollutants of different molecular weights (200–650 Dalton) and they are positively charged, negatively charged, or have no overall charge at the chosen pH of 5.8. Phenolphthalein and bromothymol blue, both pH indicators, are added to ensure an even molecular weight distribution.

Interestingly, the retention of micropollutants gives valuable information about the exclusion mechanism of the PEMs, and therefore, indirectly provides insight into the structure of the multilayer. In this study, the micropollutant retentions will be coupled to all previous results in order to develop a deeper understanding of the multilayer structure. Firstly, **Figure 5.7A** shows the micropollutant retention for [PSS/PAH]₁₀ membranes constructed at 5, 50, and 500 mM NaCl for the solid black, grey, and light grey bars respectively. The micropollutant retentions for the crosslinked membranes are shown by patterned bars on the right side of the according PEM membrane. For the non-crosslinked PSS/PAH membranes constructed at 5 mM salt, the overall retention is low and this is especially true for positively charged (+) and neutral (0) micropollutants. For the PSS/PAH multilayers constructed at 50 and 500 mM NaCl, an overall high retention towards micropollutants is observed. Especially high retentions toward positively charged atenolol and neutral micropollutants are seen. The retentions drop for negatively charged micropollutants, except for bezafibrate because of its relatively high molecular weight. After crosslinking, the retentions toward neutral and negatively charged micropollutants increases for these PSS/PAH membranes (50 and 500 mM) while the retention towards positively charged micropollutants goes down. These findings are in line with the earlier results that show that the membranes become less positively charge and denser after crosslinking (Figure 5 and 6).

For the PSS/PAS membranes (red bars in **Figure 5.7B**), the retention toward both positively and negatively charged species, i.e. atenolol (+), naproxen (–), and bezafibrate (–) are higher than one would expect from the measured MWCO of this membrane. However, the neutral micropollutants are retained less than the negative ones, which is more in line with the measured MWCO. Moreover, the complete removal of bromothymol blue indicates a defect-free separation layer. For the crosslinked PSS/PAS membrane, it is

observed that the retention toward neutral micropollutants increases, however, no increasing retention is observed toward charged micropollutants. This result is in line with the MWCO results and the ion retention results, because MWCO goes down while ion retentions change only slightly. The PSS/PEI membranes (blue bars in **Figure 5.7B**) have high retention toward every micropollutant and complete removal for naproxen (–) and bezafibrate (–) is found, indicating a high amount of dielectric exclusion occurring within this multilayer. Upon crosslinking, micropollutant retentions for the PSS/PEI membranes do not change significantly, because the PEM is already very dense.

Figure 5.7: Micropollutant retention as function of various micropollutants sorted from left to right based on their charge (left positive, middle neutral, and right negative). A: Retention of [PSS/PAH]₁₀ multilayer constructed at 5, 50, and 500 mM NaCl (black, grey, and light grey respectively). B: Retention of [PSS/PEI]₁₀ and [PSS/PAS]₁₀ multilayers in red and blue respectively. In both graphs solid bars represent non-crosslinked multilayer membranes and patterned bars crosslinked multilayer membranes. Note: CL stands for crosslinked. Error bars are standard errors from measurements on five separate membrane modules.

All three multilayer systems used in this study; PSS/PAH, PSS/PEI, and PSS/PAS are based on the same polyanion, PSS and the polycations contain crosslinkable primary amine groups. Comparison between the PEMs with different polycation is made at a building salt concentration of 50 mM NaCl. The PSS/PEI membrane is found to be the densest and least permeable with the highest overall ion and micropollutant retentions.

When the PSS/PEI multilayer is crosslinked, no change in water permeability and micropollutant retention is observed because the PEM already has a high density. The PSS/PAH membranes contain a high excess amount of PAH, and therefore, when these multilayers are crosslinked, a larger change in bulk charge is observed together with a densification of the multilayer. For the PSS/PAS membranes, a high densification of the multilayer is seen together with slightly increasing micropollutant retentions. In summary, crosslinking can be beneficial for PEM membranes to increase their performance, however, the effect of crosslinking depends strongly on the type of multilayer used.

5.4 Conclusions

In this study, the influence of polycation type (PAH, PEI, and PAS) and crosslinking on the structure and performance of PEM-coated nanofiltration membranes was investigated. PE adsorption measurements show that a 30–40% excess of PAH is present within the multilayers regardless of the building salt concentration (5, 50, and 500 mM NaCl) and this gives the membranes a positive surface charge. For the PSS/PEI and the PSS/PAS membranes, the excess amount of polycation was lower (5–11% and 10–16% respectively). Furthermore, in contrast to the PSS/PAH multilayers, these PEM membranes had a negative surface charge even though they were terminated with the polycation. At higher building salt concentrations, thicker PSS/PAH multilayers were formed and this resulted in lower water permeabilities. When the PEMs were prepared at the same salt concentration (50 mM NaCl), the PSS/PEI membranes had a 56% lower permeability than the PSS/PAH membranes, whereas the PSS/PAS has a permeability 144% higher than the PSS/PAH membranes. In addition, MWCO experiments show that the PSS/PAH ($267 \text{ g}\cdot\text{mol}^{-1}$) and the PSS/PEI ($239 \text{ g}\cdot\text{mol}^{-1}$) multilayers are dense in structure, whereas the PSS/PAS multilayers were more open with a higher MWCO ($712 \text{ g}\cdot\text{mol}^{-1}$) in line with the higher water permeability. The retention of various monovalent and divalent ions (NaCl, MgSO_4 , MgCl_2 , and Na_2SO_4) shows that the PSS/PEI and PSS/PAH membranes were dense and had high retentions toward ions. Whereas, the PSS/PAS membranes were more open than the PEI and PAH membranes, and showed clear Donnan exclusion based retentions (high Na_2SO_4 and low MgCl_2 retentions). Upon crosslinking the packing density of the PEMs increased and this effect was strongest when the PEMs were more open. Micropollutant retentions were highest for the PSS/PEI membranes which were the densest of the multilayers. Crosslinking resulted in higher

overall micropollutant retentions for all PEMs except for the PSS/PEI membranes because they were already very dense. In conclusion, this work shows the versatility of PEM membranes since with a simple change in multilayer composition, hugely different membranes can be constructed. Moreover, crosslinking of PEM-coated membranes can be hugely beneficial to increase retention toward both micropollutants and ions.

5.5 Acknowledgements

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5.6 Supplementary Information

5.6.1 Refractometry

Figure S5.1: Refractive index increment determination as function of the polyelectrolyte concentration for PSS (A), PAH (B), PEI (C), and PAS (D) measured at the according background solutions: PSS (pH=5.5 and 50 mM of NaCl); PAH (pH=2 and 50 mM of NaCl), PEI (pH=2 and 50 mM of NaCl), and PAS (pH=2 and 50 mM of NaCl).

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Chapter 6

Polyelectrolyte Multilayers for Forward Osmosis, Combining the Right Multilayer and Draw Solution

This chapter will be submitted as:

Polyelectrolyte multilayer for forward osmosis, combining the right multilayer and draw solution;
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Abstract

Polyelectrolyte multilayers (PEMs) are highly promising materials to act as selective separation layers on the inside of hollow fiber membranes and to control the chemistry of that interface. The versatility of PEM based membranes could be very relevant for forward osmosis (FO), especially in combination with the correct draw solution. In this study poly(4-styrene sulfonate) (PSS)/poly(allylamine) (PAH) or PSS/poly(ethyleneimine) based PEM membranes are used to systematically study the relation between PEM properties and their performance in FO processes. Here, the PSS/PAH PEM has a positively charged surface and bulk whereas PSS/PEI is negatively charged. For FO it was found that PSS/PAH showed the lowest reverse salt flux for MgCl_2 and MgSO_4 and for PSS/PEI this was for Na_2SO_4 and trisodium citrate (TSC). These results demonstrate that combining the right PEM with the right draw is key in getting low reverse salt fluxes in FO. Crosslinking resulted overall in a lower salt and water flux, however, the reverse salt flux selectivity was not affected. A direct comparison between NF and RO results shows that salt retentions measured in NF mode give a good indication of the magnitude of reverse salt flux in FO. When micropollutants (MPs) were retained in FO it was observed that overall high retentions are obtained except for the positively charged atenolol that showed a negative retention of -211% when using a TSC draw. The negative retentions are due to Donnan-dialysis and when a sucrose draw solution was used, atenolol retentions increased sharply to positive values because sucrose does not have any sodium ions with which the atenolol can exchange. This study demonstrates the connection between PEM structure and FO performance, but also that NF measurements can give a good indication for FO performance of PEM membranes. Furthermore, it is shown that selective exchange of charge solutes can occur due to Donnan-dialysis.

6.1 Introduction

Forward osmosis (FO) is a technique that utilizes the chemical potential difference in the form of osmotic pressure between a feed solution with low solute concentration and a draw solution with high solute concentration separated by a semipermeable membrane. [1] In this manner, water will flow from the feed solution to the draw solution in order to extract water from a contaminated stream, [2] to concentrate liquid food and beverages, [1] or to desalinate water. [3].

The benefits of FO are that no hydraulic pressure is needed and studies show that FO is less prone to fouling partly because of the higher reversibility of fouling compared to reverse osmosis (RO) type processes. [4, 5] In most FO applications it is vital to recover the draw solution and for this reason, FO always needs to have a second processing step to regenerate the draw solution. [3] The draw solution recovery can be performed via the use of waste heat in combination with a thermolytic draw solution [6] or by using a hybrid system in combination with a RO [7] or NF [8] membrane.

When looking at the mass transport within a FO process, it is found that water fluxes are lower than water fluxes measured in RO at similar osmotic and hydraulic pressures respectively. [1] The lower water flux is mainly due to concentration polarization that for FO also occurs within the support of the membrane, an effect termed internal concentration polarization (ICP). [9] Two types of ICPs exist; namely dilutive and concentrative internal concentration polarization. Here, the concentrative ICP occurs when the draw solution is facing the active layer, also called pressure retarded osmosis mode, and the dilutive ICP is a result of the support layer facing the draw solution, called FO mode. [10] In FO, this dilutive ICP substantially reduces the concentration of solutes in the support near the active layer resulting in a severe loss of driving force. [6]

These ICPs can be reduced by opening the support structure allowing the solutes of the draw solution to move more quickly through the support. [11] For FO and PRO, this is described by the structural parameter that relates the support performance to the severity of ICP. [12] The biggest opportunity to increase FO performance, when the permeability is high enough ($> 2 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$), lays in the optimization of the structural parameter that belongs to the support. [13] Furthermore, an increased selectivity of the active layer results in a better maintenance of the driving force and less loss of the draw solution, and therefore, a lower energy consumption. Because of the versatility and tunability of PEMs, PEM membranes can be an interesting option for FO in order to have high water fluxes while maintaining high selectivities in combination with the right draw solution.

Removing organic contaminants [14] or pharmaceuticals [15] using FO is a widely studied subject [16] as FO is a promising process to treat challenging waste streams due to its low fouling tendency in comparison to pressure driven processes. [17] It is even shown that rejection of organic compounds can be higher in FO in comparison to RO because of the retarded forward diffusion of solutes that results when a little reverse salt flux is present. [18] Here, the reverse salt flux hinders the forward transport of organic molecules over the active layer. Furthermore, continuing on the concept of NF membranes for FO, Alturki et al. showed that the rejection of organic contaminants in FO can be high even when NF membranes are used. [14]

With the knowledge that NF membranes in combination with the right draw can have a low reverse salt flux and a high retention toward micropollutants, polyelectrolyte multilayer (PEM) membranes could be an ideal option as an active layer because of the tunability of PEM properties like charge and density. PEMs are fabricated by alternately adsorbing oppositely charged polyelectrolytes on a charged surface and can easily be constructed on the inside of hollow fiber support membranes resulting in membranes with widely different properties. For FO, PEMs have already been investigated in numerous studies showing overall high water fluxes and moderate reverse salt flux selectivity (RSFS), though heavily depending on the type of draw solution used. The first studies used PSS/PAH multilayers coated on flat sheets [19] using a MgCl_2 draw solution, while in other work the PEM was applied on the outside of hollow fiber support membranes [20] and tested in combination with several draw solutions. A follow-up study investigated different types of multilayers in order to evaluate if PEM NF membranes are suitable for FO and found similar RSFS for PSS/PAH and PSS/PEI PEM using a MgCl_2 draw solution. [21] Other studies sought to improve the performance of PEM FO membranes by incorporating clay particles [22] or by crosslinking PSS/PAH PEMs with glutaraldehyde [23, 24] or both with glutaraldehyde and UV light. [25] All these studies showed that PEM membranes can be used for FO, however, little work has been done to understand the relation between PEM structure, like charge and density, and eventual FO performance.

In this study, two PEM membranes based on PSS/PAH and PSS/PEI, that showed in **Chapter 5** widely different properties are investigated for FO. To study the charge interactions between the PEM membrane and the draw solution, various charged draw solutions are used; (NaCl , MgCl_2 , Na_2SO_4 , MgSO_4 , and $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$). Subsequently, these PEMs are crosslinked to study the effect of crosslinking on the water and reverse salt fluxes. Finally, all PEM membranes are tested for the application of the retention of micropollutants in the FO process.

6.2 Materials and Methods

6.2.1 Materials

Branched poly(ethylene imine) (PEI, amine ratio primary, secondary, and tertiary: 1:1.2:0.76, $M_w=75,000 \text{ g}\cdot\text{mol}^{-1}$) and poly(sodium 4–styrenesulfonate) (PSS, $M_w=150,000 \text{ g}\cdot\text{mol}^{-1}$, 30 wt%. in water) were purchased from Sigma-Aldrich while poly(allylamine) (PAH, $M_w=150,000 \text{ g}\cdot\text{mol}^{-1}$, 40 wt%. in water) was purchased from Nittobo Medical, Japan. Glutaraldehyde (GA, 25 wt%. in water) was purchased from Alfa Aesar. Magnesium sulfate (MgSO_4), sodium sulfate (Na_2SO_4), trisodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$), and sucrose were purchased from Sigma-Aldrich whereas sodium chloride (NaCl) was obtained from Akzo Nobel, and magnesium chloride (MgCl_2) from Boom B.V.. Atenolol, atrazine, bisphenol A, bromothymol blue, naproxen, and phenolphthalein were purchased from Sigma-Aldrich while sulfamethoxazole was purchased from Fluka. All chemicals were used without any further purification.

Tight hollow fiber ultrafiltration membranes were obtained from NX Filtration B.V., Enschede, The Netherlands. The fibers are positively charged, have an inner diameter of 0.68 mm, a standard permeability of $200 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$, and a molecular weight cut-off of 25 kDa (pore size indicator). These hollow fiber support membranes are asymmetrical, meaning that the smallest pore sizes are present on the inside of the hollow fiber.

6.2.2 Polyelectrolyte multilayer membrane fabrication

Polyelectrolyte multilayers (PEMs) were coated on the tight hollow fiber ultrafiltration membranes described above by using the Layer-by-Layer method as described in **Chapter 5**. Two type of PEMs were coated with 10 bilayers and terminated on the polycation, a $[\text{PSS}/\text{PAH}]_{10}$ and $[\text{PSS}/\text{PEI}]_{10}$ where the former is coated at 5, 50, and 500 mM of NaCl and the latter only at 50 mM of NaCl. The pH of the coating solution for the polycations was adjusted to a pH of 2 where the pH of other solutions remained unadjusted. Subsequently, the PEM hollow fiber membrane were potted into single fiber modules with an average effective membrane length of around 19 cm.

6.2.3 Salt retention

Salt retention was measured in NF mode using various salts; NaCl, Na_2SO_4 , MgCl_2 , MgSO_4 , and $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ (trisodium citrate or TSC abbreviated) dissolved in demineralized water at a concentration of 5 mM. The measurements were performed using a crossflow setup at which an hydraulic pressure of 6.2 bars was applied at a crossflow velocity of $1 \text{ m}\cdot\text{s}^{-1}$. The

used crossflow velocity is well within the laminar flow regime with a Reynolds number of 675. The pump used in the setup is a rotary van pump (BN71B4 pump motor, Bonfiglioli, Italy; IMTI 1.5M inverter, Electroil, Italy; PA411 pump head, Fluid-o-Tech, Italy). By measuring the conductivity of the permeate and the feed, the salt retention R was determined using **Equation 6.1**.

$$R = \frac{\Delta C}{C_{\text{feed}}} \quad (6.1)$$

The salt permeability coefficient, B in $\text{m}\cdot\text{s}^{-1}$, was calculated using the solution-diffusion model [13, 26] presented in **Equation 6.2**. In this equation, J_w is the permeate water flux in $\text{m}\cdot\text{s}^{-1}$, R is the solute retention, and k is the mass transfer coefficient in $\text{m}\cdot\text{s}^{-1}$.

$$B = J_w \cdot \frac{1 - R}{R} \cdot e^{\frac{J_w}{k}} \quad (6.2)$$

In equation 2, k is the mass transfer coefficient which is the ratio between the solute diffusivity (solute diffusion coefficient in $\text{m}^2\cdot\text{s}^{-1}$) and the thickness (δ in meters) of the boundary layer at the wall of the membrane, as shown in **Equation 6.3**;

$$k = \frac{D}{\delta} \quad (6.3)$$

The mass transfer coefficient can be determined using the Lvque solution for the Sherwood relation for developed laminar flow in tubular systems [27] as shown in equation 4. Sh is the dimensionless Sherwood number describing the ratio of convective mass transport over the diffuse mass transport. Furthermore, in **Equation 6.4**, d_{in} is the inner diameter of the tube or hollow fiber in meters, L is the length of the tube in meters, Re is the dimensionless Reynolds number, and Sc the dimensionless Schmidt number as shown in **Equation 6.5** and **6.6** respectively. The Reynolds number describes the ratio of the inertial to viscous forces which is related to the turbulent and laminar motion of the fluid. In this formula, v is the crossflow velocity of the feed in $\text{m}\cdot\text{s}^{-1}$, ρ is the density in $\text{kg}\cdot\text{m}^{-3}$, and η the viscosity in $\text{Pa}\cdot\text{s}$. The viscosity over the mass diffusivity is defined by the Schmidt number and relates to the boundary layer over which mass is transported.

$$Sh = \frac{k \cdot d_{in}}{D} = 1.62 \cdot \left(Re \cdot Sc \cdot \frac{d_{in}}{L} \right)^{\frac{1}{3}} \quad (6.4)$$

$$Valid \text{ for } 100 < Re \cdot Sc \cdot \frac{d_{in}}{L} < 5000$$

$$Re = \frac{\rho \cdot v \cdot d_{in}}{\eta} \quad (6.5)$$

$$Sc = \frac{\eta}{\rho \cdot D} \quad (6.6)$$

In order to calculate the mass transfer coefficient, the diffusion coefficients of all the salts used during NF need to be known. The diffusion coefficient depends on concentration and are taken from literature at a solute concentration of 5 mM, equal to the feed concentration used in the nanofiltration experiments, all values are shown in **Table 6.1**.

Table 6.1: Diffusion coefficients of all salts at a concentration of 5 mM that are used for the retention measurements.

Type of salt	Diffusion coefficient	Reference
	(m ² ·s ⁻¹) x 10 ⁹	
	at a concentration of 5 mM	
MgCl ₂	1.14	[28]
NaCl	1.56	[29]
MgSO ₄	0.71	[30]
Na ₂ SO ₄	1.12	[31]
Na ₃ C ₆ H ₅ O ₇	1.03	[32]

6.2.4 Forward osmosis measurements

FO experiments were performed using a feed solution of demineralized water and a draw solution containing either NaCl, Na₂SO₄, MgCl₂, MgSO₄, or TSC. The feed solution was flown at the lumen side of the hollow fiber membrane facing the active layer and on the shell side the draw solution was flown. Both the feed and draw solutions were circulated using a peristaltic pump at a flow rate of 10.4 mL·min⁻¹ that translates to lumen and shell

velocities of $1 \text{ m}\cdot\text{s}^{-1}$ and $0.014 \text{ m}\cdot\text{s}^{-1}$ respectively. The conductivity was measured over time at the outlet of the feed to determine the change in salt concentration over time. The weight of the feed reservoir was measured over time to determine both the water flux and reverse salt flux, using **Equation 6.6** and **6.7** respectively. In these equations, Δm_F is the difference in mass between the mass at $t=0$ and $t=t$ in kg, ρ_F is density of the feed solution in $\text{kg}\cdot\text{L}^{-1}$, $A_{i,m}$ is the inner surface membrane area in m^2 , t is the experiment time in hours, V_F feed volume in L, and C_F is the salt concentration in the feed solution in $\text{g}\cdot\text{L}^{-1}$.

$$J_W = \frac{\Delta m_F}{\rho_F \cdot A_{i,m} \cdot t} \quad (6.6)$$

$$J_S = \frac{V_{F,t=t} \cdot C_{F,t=t} - V_{F,t=0} \cdot C_{F,t=0}}{A_{i,m} \cdot t} \quad (6.7)$$

Subsequently, knowing the water flux and the reverse salt flux, the reverse salt flux selectivity ($\text{L}\cdot\text{g}^{-1}$) can be calculated using **Equation 6.8**.

$$\text{RSFS} = \frac{J_W}{J_S} \quad (6.8)$$

The concentration of the different salts used to make the various draw solutions is such that all draw solutions have the same osmotic pressure. As a reference a 0.5 M draw solution of MgCl_2 is used, that has an osmotic pressure of 36 bar at 25°C and a subsequent water activity of 0.974. [33] In order to obtain equal osmotic pressures for every salt type, the solutions water activity should be equal, according to **Equation 6.9**. [34, 35] In this equation, Π is the osmotic pressure in bar, R is the gas constant in $\text{L}\cdot\text{bar}^{-1}\cdot\text{K}^{-1}\cdot\text{mole}^{-1}$, T the temperature in K, V_w the molar volume of water ($0.0181 \text{ L}\cdot\text{mole}^{-1}$) [36], and a_w the water activity (0.974).

$$\Pi = -\frac{RT}{V_w} \ln a_w \quad (6.9)$$

Water activities are reported in literature for every solute used in the draw solution as function of the molality for NaCl, [37] MgCl_2 , [33] MgSO_4 , [38] Na_2SO_4 , [38], TSC [37], and sucrose [39]. To convert molality into molarity **Equation 6.10** can be used where M

is the molarity in $\text{mole}\cdot\text{L}^{-1}$, m is the molality in $\text{mole}\cdot\text{kg}^{-1}$, ρ the density in $\text{kg}\cdot\text{L}^{-1}$ at the given concentration for NaCl, [40] MgCl_2 , [40] MgSO_4 , [40] Na_2SO_4 , [40] TSC, [37] and sucrose, [39] and M_w is the molar mass in $\text{kg}\cdot\text{mole}^{-1}$. In **Table 6.2** the determined concentrations in molarities are given and the corresponding literature references for the density and activity data as function of the molality used in this study.

$$M = \rho \cdot \frac{m}{1 + m \cdot M_w} \quad (6.10)$$

Table 6.2: Determined molarities of the various draw solutions calculated from the molality and density given from the corresponding literature at a water activity of 0.974 and at 25°C.

Type of salt	Molarity ($\text{mole}\cdot\text{L}^{-1}$)	Molality ($\text{mole}\cdot\text{kg}^{-1}$)	Density ($\text{kg}\cdot\text{L}^{-1}$)
MgCl_2	0.50	0.51	1.036
NaCl	0.76	0.77	1.028
MgSO_4	1.28	1.30	1.081
Na_2SO_4	0.71	0.72	1.082
$\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$	0.63	0.67	1.111
Sucrose	0.98	1.27	1.124

The structural parameter of the membrane support was determined using **Equation 6.11** [41] and the concentration polarization modulus was calculated using **Equation 6.12** [42].

$$S = \frac{D}{J_w} \ln \left(\frac{B + A \cdot \pi_{D,b}}{B + J_w + A \cdot \pi_{F,m}} \right) \quad (6.11)$$

$$\frac{\pi_{D,a}}{\pi_{D,b}} = e^{-J_w \frac{S}{D}} \quad (6.12)$$

In **Equation 6.11** and **6.12** coefficient, S is the structural parameter in meters, A the water permeability coefficient of the membrane in $\text{m}^3\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{bar}^{-1}$, B the salt permeability coefficient in $\text{m}\cdot\text{s}^{-1}$, D the diffusion coefficient in $\text{m}^2\cdot\text{s}^{-1}$, J_w the water flux in $\text{m}^3\cdot\text{m}^{-2}\cdot\text{s}^{-1}$, $\pi_{D,b}$ the bulk osmotic pressure of the draw solution in bar, $\pi_{D,A}$ the osmotic pressure at the draw side in the support at the active layer in bar, and $\pi_{F,m}$ the osmotic pressure of the feed

solution at the membrane surface in bar. The osmotic pressure, $\pi_{F,m}$, at the membrane surface of the feed solution is assumed to be zero since deionized water is used.

6.2.5 Micropollutant retention in forward osmosis

The retention of micropollutants in forward osmosis was performed by dissolving $3 \text{ mg} \cdot \text{L}^{-1}$ of each micropollutant (atenolol, atrazine, bisphenol A, bromothymol blue, naproxen, phenolphthalein, and sulfamethoxazole) in demineralized water. The feed containing the micropollutants was adjusted to a pH of 5.8 and flown through the inside (lumen) side of the hollow fiber facing the active layer in the same manner as the FO performance measurements. In order to study the effect of charge of the organic solutes, three different draw solution were used; TSC, Na_2SO_4 , and sucrose. These solutions are flown at the outside (shell) side of the hollow fiber under the same conditions as the other forward osmosis experiments described in the previous section. After 24 hours samples of the draw solution are taken and analyzed by HPLC to determine the retention of the membrane. The micropollutants permeate into a big volume, diluting the permeate sample. To compensate for this, a dilution factor (DF) is used when calculating the retention as described in a study by Alturki et al. [14], the equations are shown below by **Equation 6.13** and **6.14**. In both equations, $V_{D,t=t}$ is the final volume of draw solution, V_P is the total volume of permeated water, $C_{D,MP,t=t}$ is the final concentration of micropollutants in the draw solution, and $C_{F,t=0}$ the initial micropollutant concentration in the feed.

$$DF = \frac{V_{D,t=t}}{V_P} \quad (6.13)$$

$$R = 1 - DF \cdot \frac{C_{D,MP,t=t}}{C_{F,t=0}} \quad (6.14)$$

6.3 Results and Discussion

Here, the experimental results are shown and discussed in two sections. In the first section the forward osmosis (FO) results are discussed for two different polyelectrolyte multilayers (PEMs); [PSS/PAH]₁₀ and [PSS/PEI]₁₀ at which the PSS/PAH based PEM is built at 5, 50, and 500 mM of NaCl and PSS/PEI using 50 mM of NaCl. These membranes are tested on their FO performance in terms of water and reverse salt flux for five different draw solution; NaCl, MgSO₄, MgCl₂, Na₂SO₄, and Na₃C₆H₅O₇ (trisodium citrate, abbreviated to TSC) at equal osmotic pressure. In addition, all membranes are crosslinked in order to study for the various systems if crosslinking is beneficial for their FO performance. In the second section, the PEM membranes are tested for the application of micropollutant retention in FO using a TSC, Na₂SO₄, and sucrose draw solution. In both sections, the results will be compared to (nanofiltration) NF results from **Chapter 5** to study the connection between PEM properties and FO performance.

6.3.1 FO performance of PEM membranes using different draw solutions

The PEM membranes used are the same membranes as in **Chapter 5** in which their NF performances were measured. To obtain a good understanding how these PEM membranes perform in FO, their separation properties in NF should be first understood. For this reason, some properties obtained from the NF study like water permeability, salt retention, and zeta potential are summarized in this first part. In **Table 6.3**, the water permeability and the salt retention for the various salts are given. From these results it can be clearly seen that the permeability decreases when the salt content increases in the deposition solutions for the PSS/PAH membranes due to the formation of thicker layers. In addition, PSS/PEI shows the lowest permeability due to its denser structure in comparison to PSS/PAH as shown in **Table 6.3**. When looking at the salt retention, it is observed that for both PSS/PEI and PSS/PAH constructed at 50 mM of NaCl, MgSO₄ and TSC retention are high > 98%. However, the main difference is in the retention towards MgCl₂ and Na₂SO₄ where PSS/PAH has high retentions (> 98%) towards MgCl₂, whereas PSS/PEI has high retention (> 98%) towards Na₂SO₄. This is because PSS/PAH has a positively charged surface and bulk and PSS/PEI is negatively charged with corresponding zeta potentials of 18±6 mV and -26±9 mV respectively for the PEMs built at 50 mM of NaCl, as determined in **Chapter 5**. The NF results show that both the permeability and salt retentions differ greatly per PEM and salt concentration used in the deposition solutions.

Table 6.3: Water permeability and salt retentions for [PSS/PAH]₁₀ PEM membranes constructed at 5, 50, and 500 mM of salt and [PSS/PEI]₁₀ PEM membranes constructed at 50 mM of NaCl in NF mode. Errors are standard deviations of 5 different PEM membranes. The retention data for NaCl, MgCl₂, Na₂SO₄, and MgSO₄ are taken from Chapter 5 and retention of TSC is measured in this study.

PEM	Permeability (L·m ⁻² ·h ⁻¹ ·bar ⁻¹)	Retention NaCl (%)	Retention MgCl ₂ (%)	Retention Na ₂ SO ₄ (%)	Retention MgSO ₄ (%)	Retention TSC (%)
[PSS/PAH] ₁₀ 5 mM	22 ± 0.5	28 ± 3.0	47 ± 1.7	20 ± 0.6	28 ± 1.2	83 ± 1.4
[PSS/PAH] ₁₀ 50 mM	9.4 ± 0.1	53 ± 2.7	98.5 ± 0.17	86 ± 1.0	97.2 ± 0.13	98.8 ± 0.05
[PSS/PAH] ₁₀ 500 mM	5.8 ± 0.2	80 ± 0.5	97.9 ± 0.16	52 ± 2.0	92 ± 0.8	97.9 ± 0.16
[PSS/PEI] ₁₀ 50 mM	3.8 ± 0.2	85 ± 1.4	56 ± 0.5	99.2 ± 0.13	98.3 ± 0.56	99.4 ± 0.03

With the basic performance of the PSS/PAH and PSS/PEI PEM membranes in NF operation known, this knowledge can be used in order to interpret the FO results for the various draw solutions. As discussed in the introduction, several studies on PEM membranes for FO have used a MgCl₂ draw solution. Using MgCl₂ has the advantage that the osmotic pressure of the resulting draw solution is higher at similar molarities than the osmotic pressure produced by NaCl, as also shown in the Material and Methods section in **Table 6.2**. However, no study has yet provided a clear understanding on why certain PEM membranes are rejecting a specific draw solution well. For this reason, this study makes a much more detailed comparison between PEM structure, NF performance, and FO performance. In **Figure 6.1A** and **B**, the water and reverse salt fluxes of the PSS/PAH and PSS/PEI membranes constructed at 50 mM are plotted for various draw solutions that have equal osmotic pressures of 36 bar. These two PEMs were chosen for comparison because of their distinctive difference in bulk and surface charge and the according salt retention behavior, as also demonstrated in **Table 6.3**. Focusing first on the reverse salt fluxes, it is observed that the reverse salt flux for PSS/PAH is the lowest for a MgCl₂ draw solution (7.9 g·m⁻²·h⁻¹). The divalent cation, Mg²⁺, can be better rejected by PSS/PAH based PEM membranes due to high amount of positive charge present within that specific PEM [43, 44], as also described in the previous section. For PSS/PEI, which is negatively charged, the lowest reverse salt fluxes are found for Na₂SO₄ (5.2 g·m⁻²·h⁻¹) and TSC (1.1

$\text{g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$) draw solutions. The negative multivalent anions in these draws are repelled very well by the negatively charged PSS/PEI PEM membrane.

Regarding NaCl, the most commonly used draw solution in literature, it is seen that for both PEMs, the NaCl reverse salt flux is very high with a salt flux of $> 300 \text{ g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ for PSS/PAH and $> 200 \text{ g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ for PSS/PEI, as expected for NF type membranes. For PSS/PAH, the reverse salt flux for Na_2SO_4 is the highest after NaCl due to the positive charge of the PEM. However, overall there is no extreme variation between the reverse salt fluxes of multivalent anion or cation containing salt types, indicative of dielectric-exclusion for PSS/PAH membranes. For the PSS/PEI membranes, a more charge dependent reverse salt flux behavior is observed with a very high MgCl_2 salt flux ($101 \text{ g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$) in comparison to very low fluxes for salts containing a multivalent anion, indicating a more Donnan-exclusion type of behavior. It is noticed that the reverse MgSO_4 flux for both PEMs is higher than the MgCl_2 or Na_2SO_4 reverse salt flux for PSS/PAH and PSS/PEI respectively that have a low reverse salt flux. This is probably due to MgSO_4 having a divalent cation as well as a divalent anion, since PSS/PAH is positively charged, the sulfate will have a higher affinity for the PEM that can drag the magnesium along. The reverse argument holds for the PSS/PEI PEM with a MgSO_4 draw, while with only Na_2SO_4 this does not happen since sodium is a monovalent cation.

The results from the reverse salt fluxes for both multilayers are in line with the known surface and bulk charge from **Chapter 5** of the PEM based membranes and the salt retention results obtained in NF. Clearly salt rejection results obtained in NF mode provide a good prediction for the reverse salt fluxes in FO mode. Moreover, these results show that it is crucial to couple the right draw solution to the appropriate PEM in order to obtain low reverse salt fluxes.

Figure 6.1: Water fluxes (solid bars on the left y-axis's) and salt fluxes (patterned bars on the right y-axis's) of various FO measurements at which a demineralized feed was used facing the active layer (FS-AL) and a draws solution with an osmotic pressure of 36 bar. PSS/PAH (A) and PSS/PEI (B) PEM membranes built at 50 mM tested for various draw solutions at equal osmotic pressures. Error bars are standard deviations of 5 different PEM membranes.

The water fluxes for the PSS/PAH and PSS/PEI based PEM membranes in FO mode using various draw solutions are also shown in **Figure 6.1**. Here, it is observed that the water flux varies for every draw solution and PEM type, although the osmotic pressures of 36 bar for all draws are equal. In FO, besides the resistance in the active layer, dilutive ICP, and the magnitude of the reverse salt flux all determine the resistance, and therefore, the water flux. Where the permeability plays an important role when the water fluxes are low ($< 2 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$), the interplay between the structural parameter (described in **Equation 6.10**), type of salt, and the reverse salt flux determine the main water fluxes in FO. This can be seen for PSS/PAH with a NaCl draw and PSS/PEI for NaCl, MgSO_4 , and MgCl_2 draw solution. With these draws, the salt flux is relatively high and the water flux relatively low in comparison to other draw solutions. This is most likely due to a loss in driving force because of the high reverse salt flux. For draw solutions that have a low reverse salt flux, it is indeed observed that the water fluxes are relatively higher. Here, Na_2SO_4 , TSC, and MgCl_2 (only for PSS/PAH) show the right combination of low reverse salt flux and high water flux. This indicates that a draw is needed that is small enough to have a high diffusion but also big enough to be retained. This trade-off can be observed for PSS/PEI using a TSC and Na_2SO_4 draw where the former has a lower reverse salt flux but also a lower water flux.

The main resistance in a FO membrane can be quantified by the structural parameter as shown in **Equation 6.10** that encompasses all the main resistances of the FO membrane. Moreover, this huge support resistance can be made more tangible by showing the difference between FO and NF, where the same water fluxes in NF can be obtained using only 2-4 bar of hydraulic pressure depending on the PEM type instead of 36 bar of osmotic pressure. The structural parameter of the supports used in this study for the PSS/PAH and PSS/PEI membranes constructed at 50 mM of NaCl are given in **Table 6.4**. From the different structural parameters it is seen that the value is ranging from 300-950 μm varying a bit per PEM and type of draw solution used. The corresponding concentration polarization modulus, calculated using **Equation 6.11**, is between 0.07 and 0.21 meaning that the osmotic pressure at the surface of the active layer is magnitudes lower than the bulk osmotic pressure, indicating a large dilutive ICP. In addition, the different diffusion coefficients of the separate draw solutions also have an influence on the severity of ICP. One of the possible reasons that the variance of the structural parameter is so large for the different PEM membranes is that the inside of support is also coated during the PEM fabrication process. This influences the affinity of the support toward the different draw solutions resulting in different structural parameters. Moreover, it was already discussed that the assumption of the solute concentration at the feed side of the membrane surface is zero is not completely true for PEM membranes. Since the reverse salt flux depends on the type of PEM and the type of draw solution, the structural parameters will therefore also vary. A higher reverse salt flux will lead to an overestimation of the structural parameter.

Table 6.4: Structural parameter for different draw solutions of the [PSS/PAH]₁₀ and [PSS/PEI]₁₀ PEM membranes. Errors are standard deviations from five different PEM membranes.

Type of salt	Structural parameter (μm) [PSS/PAH] ₁₀ – 50 mM	Structural parameter (μm) [PSS/PEI] ₁₀ – 50 mM
MgCl ₂	466 ± 172	440 ± 157
NaCl	907 ± 330	634 ± 208
MgSO ₄	487 ± 112	429 ± 234
Na ₂ SO ₄	395 ± 117	301 ± 118
Na ₃ C ₆ H ₅ O ₇ (TSC)	518 ± 121	352 ± 90

The salt concentration during PEM buildup can have significant effects on PEM properties. Here we focus on PSS/PAH and the influence on FO performance on the difference in salt concentration used during buildup. The comparison is made using two different draw solutions, namely MgCl_2 and TSC, and with the PSS/PEI PEM as shown in **Figure 6.2A** and **B**. From our previous NF study in **Chapter 5** it is known that the PEM built at 5 mM of NaCl has defects and in this study it is seen the reverse salt flux becomes much lower when the PEM is built at either 50 or 500 mM of salt due to the PEM becoming defect-free. Interestingly, looking at **Figure 6.2A**, for a MgCl_2 draw solution the water flux is the lowest for the defective membrane indicating, as already mentioned in the previous section, that a too high reverse salt flux causes a loss in driving force. This behavior can also be observed when PSS/PAH is compared to PSS/PEI, where PSS/PEI has a higher reverse MgCl_2 flux than PSS/PAH PEM membranes, resulting in a relative lower water fluxes.

Moving on to **Figure 6.2B**, a TSC solution is used as the draw instead of MgCl_2 . For the PSS/PAH based membranes it is observed that the reverse salt flux for the 50 and 500 mM constructed PEMs is relatively low and the water flux clearly decreases with increasing salt concentration due to the increase in PEM thickness. [45] This is something not observed for the MgCl_2 draw solution due to the high reverse salt flux for the PEM constructed at 5 mM. For the TSC draw solution, it is observed that the water fluxes are relatively similar to the MgCl_2 draw solution and are around $20 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ independent of the type of PEM. Overall, in comparison with other FO membranes in literature, the PEM membranes show water fluxes that are on the high side of around $20 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ of what is reported. [46]

Figure 6.2: Water fluxes (solid bars on the left y-axis's) and salt fluxes (patterned bars on the right y-axis's) of various FO measurements at which a demineralized feed was used facing the active layer (FS-AL) and a draws solution with an osmotic pressure of 36 bar. Using MgCl_2 (A) as a draw solution and TSC (B) for PSS/PAH (built at 5, 50, and 500 mM, black columns) and PSS/PEI (built at 50 mM, blue columns). Error bars are standard deviations of 5 different PEM membranes.

Subsequently we studied if crosslinking can improve the FO performance of the used PEM membranes, as shown in **Figure 6.3** for PSS/PAH (A) and PSS/PEI (B). Here, the salt flux against the water flux is plotted to study the influence of crosslinking on both fluxes. For PSS/PAH PEM membranes it is known from **Chapter 5**, as also shown in **Table 6.5**, that the salt retention in NF mode towards anions increases upon crosslinking with glutaraldehyde. Similar behavior is observed for the FO performance at which the reverse salt flux goes down for both Na_2SO_4 MgSO_4 , and TSC while the reverse salt flux for MgCl_2 remains unaltered. For PSS/PEI, shown in **Figure 6.3B**, it is measured that in general the water flux decreases and that all salt fluxes, except the TSC flux, go down upon crosslinking, less in line with the salt retention measured in NF mode in **Table 6.5**, where only an increased retention for MgCl_2 was observed. Important to note is that for the PSS/PEI system, the MgCl_2 results are excluded from the figure because the salt fluxes (101 and $52 \text{ g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ for a non- and crosslinked PSS/PEI PEM membrane respectively at water fluxes of 15 and $14.7 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$) are too high for a clear comparison to PSS/PAH.

Table 6.5: Water permeability and salt retentions for crosslinked (CL) PEM membranes for [PSS/PAH]₁₀ and [PSS/PEI]₁₀ PEMs constructed at 50 mM of NaCl in NF mode. Errors are standard deviations of 5 different PEM membranes. The retention data for NaCl, MgCl₂, Na₂SO₄, and MgSO₄ are taken from Chapter 5 and retention of TSC is measured in this study. Grey rows are the data for the crosslinked PEM membranes (CL).

Crosslinked PEM – NF	Permeability (L·m ⁻² ·h ⁻¹ · bar ⁻¹)	Retention NaCl (%)	Retention MgCl ₂ (%)	Retention Na ₂ SO ₄ (%)	Retention MgSO ₄ (%)	Retention TSC (%)
[PSS/PAH] ₁₀	9.4 ± 0.1	53 ± 2.7	98.5 ± 0.17	86 ± 1.0	97.2 ± 0.13	98.8 ± 0.05
50 mM	CL: 7.5 ± 0.3	50 ± 1.5	97 ± 0.5	98.4 ± 0.63	98.6 ± 0.46	99.2 ± 0.07
[PSS/PEI] ₁₀	3.8 ± 0.2	85 ± 1.4	56 ± 0.5	99.2 ± 0.13	98.3 ± 0.56	99.4 ± 0.03
50 mM	CL: 3.5 ± 0.1	89 ± 1.0	73 ± 1.1	99.1 ± 0.09	98.8 ± 0.17	99.6 ± 0.01

When the water and salt fluxes are known, the reverse salt flux selectivity (RSFS) can be determined, as described by **Equation 6.8**. The RSFS (L·g⁻¹) is the ratio between the water and reverse salt flux and tells how much water has permeated per mass of draw solution lost. For both PSS/PAH and PSS/PEI it is determined that no significant increase in RSFS is observed upon crosslinking due to both water and salt fluxes going down. Overall, it depends per PEM and type of draw solution which effect crosslinking has on a PEM membrane in FO. Although crosslinking has no pronounced effect on selectivity, it could still be of interest to lower the reverse salt flux which is possible for some PEM and draw solution combination. Moreover, it is most likely that crosslinking has a beneficial effect on the stability of the PEM membrane.

Figure 6.3: Salt flux as function of the water flux for PSS/PAH (A) and PSS/PEI (B) PEM membranes for a variety of draw solutions: MgSO_4 blue and square symbols; MgCl_2 black and triangle symbols; Na_2SO_4 green and diamond symbols; and TSC yellow and circle symbols. The non-crosslinked (non-CL) PEM membranes have solid symbols and the crosslinked (CL) PEM membranes have open symbols.

To summarize this section about the FO performance of PEM membranes using different draw solutions. When NF performances are compared to FO performances in terms of water and reverse salt flux for PEM membranes, the trends are similar. This especially means that when a high retention ($> 98\%$) is measured for a certain type of multivalent salt in NF, this will result in a low reverse salt flux in FO. However, for NaCl this trend cannot be concluded since a NF retention of 85% for the PSS/PEI PEM membrane still resulted in a reverse salt flux higher than $200 \text{ g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$. This demonstrates again that the interplay between the draw type and type of PEM is key for obtaining good FO results. From this comparison it can be concluded that NF salt retention measurements can be a good indication for the amount of reverse salt flux. In addition, to accomplish a low reverse salt flux below $1.1 \text{ g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ with PEM membranes, a salt retention of at least 99% should be measured in NF experiments, for example the retention and reverse salt flux for TSC using a PSS/PEI PEM membrane.

6.3.1.1 PEM membranes for the separation of micropollutants in FO

In the previous part, the relation between PEM structure and FO performance has been studied. In the next step, the constructed PSS/PAH and PSS/PEI based PEM membranes

are evaluated on their ability to reject micropollutants (MPs) in FO operation when different draw solutions are used. In this study, MPs that are emerging in our water bodies [47] are used in order to test how well these contaminants can be removed by FO using PEM membranes. The mix contains different MPs that vary in molecular weight (200–650 Dalton) and charge; being either negatively, positively, or uncharged at the chosen pH of 5.8. The mix also contains two pH indicators; phenolphthalein and bromothymol blue for an even molecular weight distribution. For this part, only the PSS/PEI PEM membranes were used in either crosslinked and non-crosslinked form, since these showed the highest retention in NF mode shown in **Figure 6.4**.

Figure 6.4: Retention of micropollutants by non-crosslinked (solid columns) and crosslinked (patterned columns) [PSS/PEI]₁₀ PEM membranes in NF at an hydraulic pressure of 6.2 bar and a crossflow velocity of 1 m·s⁻¹. Error bars are standard errors from five different membrane samples.

The MP retention shown in **Figure 6.4** is measured in NF mode for a non-crosslinked and crosslinked PSS/PEI PEM membrane and it can be seen that overall high retentions are obtained. Moreover, no distinct difference is seen between the overall MP retention of the non-crosslinked and crosslinked PEM membrane, a similar trend as the RSFS. When looking at the similar trends shown for the reverse salt fluxes with respect to the salt retentions, it is expected that the MP retention in FO is also high for a PSS/PEI based PEM membranes. In addition, it could be that the MP retention in FO is even higher since the reverse salt flux can have a positive influence on the retention of organic solutes due to

retarded forward diffusion. [18] Unfortunately, using the setup in this study, the MP retention could only be measured by taking samples from the draw solution. This means that the already low concentration of MPs is further diluted by the volume of the draw solution. In **Table 6.6**, the MP retention in FO for non-crosslinked and crosslinked PSS/PEI PEM membranes is given. Due to the dilution of MPs, the detection limit (DL) resulting from the limit of detection (LOD) is given for all MPs except atenolol and atrazine (for the non-crosslinked PEM).

Table 6.6: Retention of micropollutants by non-crosslinked and crosslinked [PSS/PEI]₁₀ PEM membranes in FO using a TSC draw solution with an osmotic pressure of 36 bar. Errors are standard deviations from three different membrane samples in FO and five different membrane samples in NF mode.

	[PSS/PEI] ₁₀		[PSS/PEI] ₁₀ – Crosslinked	
	NF retention	FO retention	NF retention	FO retention
Atenolol	94±0.2%	-211±25%	97±0.2%	-239±33%
Atrazine	98.4±0.13%	91±0.9%	97.5±0.23%	>90%
Bisphenol A	94±0.4%	>87%	94±0.4%	>93%
Phenolphthalein	97.9±0.21%	>88%	98.3±0.24%	>84%
Bromothymol blue	100%	>77%	100%	>70%
Sulfamethoxazole	95±0.3%	>88%	92±0.3%	>85%
Naproxen	100%	>88%	99.0±0.14%	>85%
Bezafibrate	99.9±0.02%	>91%	99.8±0.12%	>88%

Table 6.6 shows that except for atenolol, the overall MP retention is at least above the detection limit of around 90%, meaning that also in FO most MPs are retained very well by the PEM membranes. The difference in LOD is due to the varying dilution factors because the PEMs have different water fluxes. The lower LOD with respect to retention, due to accounting for the dilution factor, does not allow a fair comparison to the MP retention in NF mode. Interestingly, the retention of atenolol using TSC as the draw solution is -211%, meaning that the forward flux of atenolol is higher than the water flux. We attribute this observation to a phenomenon called Donnan-dialysis. In this case it means that the positively charged atenolol is exchanged with the sodium ions in the TSC draw solution due to the negative bulk and surface charge of the PSS/PEI PEM membrane. [48] Since the concentration of sodium ions is very high in the draw, a rapid exchange between atenolol occurs leading to such high forward fluxes of atenolol. Since Donnan-

dialysis is a process in which, in this case, the individual cations are transported, a way to prove that Donnan-dialysis is happening is by comparing to another MP (atrazine) that is uncharged, is still in the limit of detection, and by changing the draw solution.

The draw solution is changed from TSC to Na_2SO_4 and sucrose as shown in **Figure 6.5**. The retention of atrazine should not be affected by changing the draw solution since no ions can exchange due to the lack of charge. However, for atenolol no difference should be seen between TSC and Na_2SO_4 since for both the exchange is governed by the sodium ions. [49] When the draw is changed to sucrose, any form of cation-atenolol exchange should be disabled and retentions should increase. When looking at **Figure 6.5**, the hypothesis described above is correct and the retention of atenolol does not change when Na_2SO_4 is used. However, the atenolol retention increases sharply to 55% for the non-crosslinked PSS/PEI PEM membrane when sucrose is used as a draw. Although a sharp difference was observed in the atenolol retention, no change was measured for the retention of atrazine. This indicates that a selective Donnan-dialysis takes place for atenolol when a TSC and Na_2SO_4 draw solution is used.

To summarize, generally MPs are still rejected well with retentions above 90% in FO when a PSS/PEI based PEM membrane is used. When no Donnan-dialysis occurs, the retention for MPs is in line with the ones measured in NF mode, which can therefore give an indication for MP retention in FO. However, it is also observed that for atenolol, the positively charged MP, Donnan-dialysis occurs when draw solutions are used containing sodium ions due to the PSS/PEI PEM having a negative surface and bulk charge. When a draw solution of sucrose is used, atenolol retention increases sharply to positive values while unaffected other MP retentions. This creates the possibility of separating selectively positively, negatively, and uncharged organic solutes from each other.

Figure 2: Atenolol (blue columns) and atrazine (pink columns) retention for a [PSS/PEI]₁₀ PEM membrane using a TSC, Na₂SO₄, and sucrose draw solution at equal osmotic pressure. Error bars are standard deviations of three different membrane samples.

6.4 Conclusion

This work described here highlights the clear connection between PEM properties and FO performance and demonstrates that PEM based membranes can perform well in a FO process. FO performance depends heavily on the right combination of PEM and draw solution to obtain low reverse salt fluxes and high water fluxes. Two types of PEMs were investigated; PSS/PAH and PSS/PEI where the bulk and surface charge of the first is positive and the second negative. The overall charge of the PEM is found to be crucial for the choice of draw solution where low salt fluxes were obtained with TSC and Na₂SO₄ using a PSS/PEI PEM membrane and MgCl₂ and MgSO₄ using a PSS/PAH PEM membrane. The water fluxes measured in FO for PEM membranes are relatively high and it depends on the interplay of PEM type and draw solution if high water and low reverse salt fluxes can be obtained. Permeability tests in NF do not follow the same trend with respect to the water fluxes as measured in FO. On the other hand, salt retentions measured in NF are a good indication of reverse salt fluxes in FO and when salt retentions above 99% are obtained, reverse salt fluxes measured are as low as 1.1 g·m⁻²·h⁻¹. Crosslinking was demonstrated to lower the water and reverse salt fluxes, however, the reverse salt flux selectivity was not affected. The rejection of MPs from the feed stream using FO shows that, except for atenolol, MPs are rejected at least above 90%, in line with retentions measured in NF mode. For the positively charged atenolol, negative retention of -211%

was measured using a PSS/PEI PEM membrane and a TSC and Na_2SO_4 draw solution. The negative retention is due to Donnan–dialysis occurring where the atenolol is exchanged by the sodium ions of the draw solution. When the draw solution was changed to the non-electrolyte containing sucrose, retention for atenolol increased sharply to positive values. This work shows, therefore, for the first time that Donnan–dialysis occurs with PEM membranes in FO and can be used to separate different charged species from the feed stream using PEM membranes.

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Chapter 7

Aquaporin containing proteopolymersomes in polyelectrolyte multilayer membranes

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Abstract

The field of membranes has seen huge developments in the last decades with the introduction of both polyelectrolyte multilayer (PEM) based membranes and biomimetic membranes. In this work, we combine these two promising systems and demonstrate that proteopolymersomes (PP+) with the incorporated Aquaporin protein can be distributed in a controlled fashion using PEMs, even on the inner surface of a hollow fiber membrane. In this way, various proteopolymersome multilayers (PPMs) are fabricated using PP+ as the positively charged species in combination with the polyanions PSS and PAA. It is shown by reflectometry through alternately adsorbing the polyanions and PP+, that for both PAA and PSS a good layer growth is possible. However, when the multilayers are imaged by SEM, the PAA based PPMs show dewetting whereas vesicular structures can only be clearly observed in and on the PSS based PPMs. In addition, membrane permeability decreases upon coating the PPMs to $2.6 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ for PAA/PP+ and $7.7 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ for PSS/PP+. Salt retentions show that PAA/PP+ layers are defective (salt retentions <10% and high MWCO), in line with the observed dewetting behavior, while PPMs based on PSS show 80% MgSO_4 retention in combination with a low MWCO. The PSS/PP+ membranes show a Donnan-exclusion behavior with moderate MgCl_2 retention (50-55%) and high Na_2SO_4 retention (85-90%) indicating a high amount of negative charge present within the PPMs. The corresponding PEMs on the other hand, are predominately positively charged with MgCl_2 retention of 97-98% and Na_2SO_4 retention of 57-80%. This means that the charge inside the multilayer, and thus its separation behavior, can be changed when PP+ is used instead of a polycation. When comparing the PPM membranes to literature, similar performances are observed with other biomimetic membranes that are not based on interfacial polymerization, but these are the only ones prepared using a desired hollow fiber geometry. Combining PEMs and biomimetic approaches can thus lead to relevant membranes, especially adding to the versatility of both systems.

7.1 Introduction

The field of membranes has seen huge developments in the last decades with the arrival of novel promising membranes like polyelectrolyte multilayer (PEM) based membranes and biomimetic membranes. Both PEM based membranes and biomimetic membranes have been investigated in a variety of studies and both are already commercially produced and applied [1].

PEMs are fabricated using two oppositely charged polyelectrolytes that are adsorbed alternately on top of a charged surface [2]. Using PEMs, membranes can be fabricated by applying the PEMs on top of a porous support membrane. Using this coating method, PEM membranes have been studied for numerous applications regarding water purification, e.g., for reverse osmosis (RO) [3], forward osmosis (FO) [4], and nanofiltration (NF) [5] processes. However, when looking at these processes in more detail, PEM membranes are not really competitive as RO membranes, as they can only be made selective enough for RO at a huge cost of permeability [3, 5]. Due to the low permeability of PEM based RO membranes, these type of membranes currently do not outperform polyamide based RO membranes. However, their relatively high permeability and the tunability of their selectivity make that PEMs are ideal candidates for NF membranes. In addition, PEMs can be easily coated on the inside of hollow fibers allowing manufactures to produces modules with a higher aspect ratio and without spacers which are prone to fouling [6]. PEM membranes can, furthermore, be easily cleaned due to their high chemical and physical stability, especially in comparison to polyamide based membranes [7].

Biomimetic membranes are a collection of membranes which are inspired by biological membranes present in the walls of cells [8]. One type of biomimetic membranes is based on the aquaporin protein which acts as a selective water channel and allows water molecules to pass up to one billion molecules per second per channel [9]. The water molecules pass the ultra-narrow hydrophobic channel by moving in a single file, allowing for the passage of water while retaining all other solutes [10]. This high selectivity toward water is due to the size restriction, charge repulsion [11], and the specific dipole orientation of water [12] within the aquaporin water channel. For the reasons above, the aquaporin water channel is very promising since in RO and NF operations high selectivities are needed which could be obtained with these channels on the condition that water is only permeating through the aquaporin channels [13]. Moreover, due to the high throughput of water molecules, the permeability of both NF and RO membranes can potentially be increased [14].

In order to retain the structure and function of the aquaporin water channel, the protein has to be reconstituted into an phospholipid bilayer [15] or an amphiphilic block copolymer bilayer [16, 17]. This can be achieved by embedding the aquaporin proteins into vesicles, i.e. liposomes or polymersomes. Of the two, polymersomes show a higher physical and chemical stability [18] and a tunable thickness and permeability [19]. To make membranes that contain the aquaporin protein, two approaches have been studied; namely the supported bilayers [18] and the vesicle embedded membranes[20, 21]. Although supported bilayers show higher permeabilities, they are prone to mechanical damage and degradation and are highly difficult to produce in a defect free manner. For this reason, vesicle embedded membranes will be used in this study since the vesicles can easily be incorporated into an existing layer that supports the vesicles and prevents defects [14]. Moreover, Górecki et al. showed that aquaporin containing proteopolymersomes have been successfully added to polyamide layers, where they contributed to an improved membrane performance [22].

Looking at both approaches, combining biomimetic membranes with PEMs is interesting because of the high selectivity and permeability of aquaporin water channels and the tunability of PEMs. Moreover, by relying on electrostatic interactions with polyelectrolytes (PEs), aquaporin containing proteoliposomes or proteopolymersomes can be easily distributed to form a layer with a high packing density of vesicles. Previous studies already reported how to distribute aquaporin containing vesicles using magnetic particles inside the vesicles [23], by interaction with PEs [24], by mixing them in the aqueous phase during interfacial polymerization [20], or by incubating the substrate.[21] In this way, these studies controlled the vesicle distribution on the surface and constructed membranes with visible vesicles on the surface. However, to asses the vesicles distribution, simple methods are missing in order to quantify the amount of vesicles within the active layer of the membrane. Therefore, in this study aquaporin containing proteopolymersomes will be adsorbed in a controlled manner on model surfaces to study the growth of vesicles containing multilayers and translate this knowledge to allow controlled layer formation on the inner surface of hollow fiber membranes. There have been published studies and patents reporting proteoliposomes/proteopolymersomes on the inside of an hollow fiber configuration, however, this was all performed using interfacial polymerization (IP) [25-28]. The IP fabrication method is hard to control on an hollow fiber geometry, therefore, a more straightforward method to produce hollow fiber based biomimetic membranes would be very beneficial.

In this study, we therefore propose a simple method to form hollow fiber proteopolymersome multilayer (PPM) membranes based on sequential dip-coating of PEs and proteopolymersomes (PP+). The PPMs are based on three different multilayers varying in interaction between weak and strong PEs; poly(acrylic acid) (PAA)/poly(allyl amine) (PAH) [29], poly(styrene 4-sulfonate) (PSS)/PAH [30], and PSS/poly(diallyl dimethyl ammonium chloride) PDADMAC [31]. PAA/PAH multilayers consist of two weak PEs resulting in a dense layer (low MWCO) with low permeability, but also low salt retentions [32]. Changing the polyanion from a weak to a strong PE creating a PSS/PAH multilayer, results in a totally different multilayer with both high permeabilities and high salt retentions [33]. When the polycation is subsequently switched from weak to strong, a PSS/PDADMAC multilayer is fabricated with high permeabilities and moderate salt retentions, but with an excellent chemical stability due to the quaternary amine of PDADMAC [7]. The polycations in the mentioned PEMs are simply substituted by the PP+ to build a PPM, fabricating in essence two different PPMs; a PAA/PP+ and a PSS/PP+ PPM. Here, the fabricated PPMs are compared with the traditional PEMs to obtain a deeper understanding how the PP+ affect the composition of the multilayer, and therefore, how they affect the performance of the membrane. It is shown by studying the PPM growth on model surfaces with reflectometry that PPMs can be grown in combination with different polyanions. On the inside of hollow fiber membranes, using SEM and membrane performance measurements it is further shown that the PPM layers can be fabricated and used as an active layer. Subsequently, the nanofiltration performance of the membranes is tested and compared to the original PEMs without any PP+ and to values reported in literature.

7.2 Materials and Methods

7.2.1 Materials

Poly(diallyldimethylammonium chloride) (PDADMAC, $M_w=200,000\text{--}350,000\text{ g}\cdot\text{mol}^{-1}$, 20 wt.% in water), poly(sodium 4-styrenesulfonate) (PSS, $M_w=200,000\text{ g}\cdot\text{mol}^{-1}$, 30 wt.% in water), and poly(acrylic acid) (PAA, $M_w=250,000\text{ g}\cdot\text{mol}^{-1}$, 35 wt.% in water) were purchased from Sigma-Aldrich and poly(allylamine hydrochloric acid) (PAH, $M_w=150,000\text{ g}\cdot\text{mol}^{-1}$, 40 wt.% in water) was obtained from Nittobo Medical, Japan. Sodium chloride was purchased from Akzo Nobel, magnesium chloride and magnesium sulfate were purchased from Boom B.V., and sodium sulfate from Sigma-Aldrich.

Proteopolymersomes (PP+) were obtained from Aquaporin A/S, Denmark. PP+ consisted of a 1.12 mg/mL mixture of poly(2-methyl-2-oxazoline)-block-poly(dimethylsiloxane) (PMOXA-PDMS) diblock copolymer, poly(2-methyl-2-oxazoline)-*block*-poly(dimethylsiloxane)-*block*-poly(2-methyl-2-oxazoline) (PMOXA-PDMS-PMOXA) triblock copolymer and bis(3-aminopropyl) terminated poly(dimethylsiloxane) (A-PDMS) in phosphate buffered saline (PBS) with 0.05% Lauryldimethylamine N-oxide (LDAO), 0.5% Kolliphor® HS 15 (KHS) and 5 mg/L of Aquaporin Z protein. They were prepared via bulk hydration self-assembly, according to procedures described by M. Spulber et al. [34] and in a study by Górecki et al. [22] The average particle size of PP+ was reported to be 150 ± 1 nm with total particle concentration of $3.26 \times 10^{11} \pm 7.08 \times 10^9$ particles/mL, and a neutral to slightly positive ζ -potential ($+ 0.9$ mV) due to the A-PDMS.

Obtained PP+ were filtered by a 0.4 μm Whatman filter prior to use. To check the PP+ solution quality, filtered solution was measured by Dynamic Light Scattering (DLS) Zetasizer Nano Zs (Malvern, United Kingdom) – if a $> 85\%$ intensity peak at 150-250 nm was observed, then the solution was recognized as good quality [22].

Tight ultrafiltration hollow fiber membranes were obtained from NX Filtration B.V. (Enschede, the Netherlands) and are used as supports. The charge of the supports is positive, the inner diameter is 0.68 mm, the standard permeability is $200 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$, and the fibers have a molecular weight cut-off of 25 kDa. The radial structure of the hollow fibers is asymmetrical inside-out, meaning that the smallest pore size is present on the inside of the fiber. Silicon wafers were obtained from WaferNet Inc. (San Jose, USA).

7.2.2 Reflectometry

The buildup of polyelectrolyte multilayers (PEMs) and PP+ multilayers was measured quantitatively using optical fixed angle reflectometry on top of a silicon wafer with a top layer of 80 nm silicon oxide. All polyelectrolyte (PE) solutions contain $0.1 \text{ g}\cdot\text{L}^{-1}$ of PE, 50 mM of NaCl, and were adjusted to a pH of 2 for PAH, pH of 6 for PAA, and no pH adjustment for PDADMAC and PSS. The PP+ solutions were not adjusted for the pH and no additional salt was added. Rinsing solutions contained the same ionic strength as the PE solutions with no pH adjustment.

Prior to the measurement, silicon wafers were oxygen plasma treated by a Femto plasma cleaner (Diener electronic GmbH, Germany) to clean and to obtain a reproducible SiO_2 surface chemistry. Subsequently, the wafer was put into the reflectometry flow cell while the rinsing solvent was flowing. The first layer is a layer of PAH to create a stable primer layer in order to grow the PPM. The first layer was adsorbed by flowing a PAH solution

onto the silicon wafer until a stable adsorption plateau was reached. After the first layer the rinsing solution was flown until the adsorption was stable. Subsequently, the second layer was adsorbed by flowing either a PSS or PAA solution. After rinsing, the PP+ solution was flown and by alternately adsorbing a polyanion (PSS or PAA) and the PP+ solution with rinsing steps in between, a PPM could be built. All experiments took place under ambient conditions.

Reflectometry uses monochromatic light (He-Ne laser, 628.8 nm) which is linearly polarized. The laser beam is reflected from the silicon wafer at an angle of 71°, also known as the Brewster angle. In the detector the laser light is split into its parallel and perpendicular components. **Equation 7.1** shows that the difference of these components divided by the initial state is proportional to the amount of mass adsorbed on top of the silicon wafer.

$$\Gamma = Q \cdot \frac{\Delta S}{S_0} \quad (7.1)$$

In **Equation 1**, Γ is the amount of mass adsorption on the silicon wafer in $\text{mg}\cdot\text{m}^{-2}$. ΔS is the signal difference between the parallel and perpendicular component and S_0 is the initial signal. Q is known as the Q-factor or sensitivity factor and depends on the refractive indices, thickness of the silicon oxide layer and adsorbed layers, angle of incidence, and the refractive index increment of the multilayer. An optical model was used to estimate the sensitivity factor of a PPM on top of a silicon wafer with 80 nm of silicon oxide. The sensitivity factors were calculated to be 24 and 25 $\text{mg}\cdot\text{m}^{-2}$ for PAA/PAH and PSS/PAH multilayers respectively. For the according PPMs, the same sensitivity factors were used in order to calculate the adsorption.

7.2.3 Scanning electron microscopy

Surface and cross-sections images were taken by a field emission scanning electron microscope (JSM-7610F, JEOL, Japan). Prior to imaging, the samples were sputter coated (Quorum Q150T ES, United Kingdom) by a 5 nm thick chromium layer. All samples were dried in a vacuum oven prior to sputter coating and the images were taken with an accelerating voltage of 1.0 kV.

7.2.4 Transmission electron microscopy

Solution samples containing proteopolymersome were introduced onto the carbon grid. Subsequently, the solution on the grid was incubated for 5 minutes, excess solution was

then drained off the bottom of the carbon grid using a filter paper after. The sample was washed by deionized water and stained by adding an aqueous solution containing 1% of phosphotungstic acid. Excess solution was again drained from the bottom of the carbon grid using a filter paper. Imaging was conducted using a 200 kV JEM-2100F Transmission Electron Microscope (JEOL, USA).

7.2.5 Membrane performance experiments

For hollow fiber membrane performance measurements, the coated hollow fiber membranes were potted into single fiber modules using PE tubing with a 6 mm outer diameter. A crossflow setup in which hydraulic pressure is applied by a rotary vane pump (BN71B4 pump motor, Bonfiglioli, Italy; IMTI 1.5M inverter, Electroil, Italy; PA411 pump head, Fluid-o-Tech, Italy) is used to perform permeability and salt retention measurements

The permeability was measured using demineralized water in a crossflow setup at an applied transmembrane pressure of 2 bars. At least 10 mL of permeate is collected before measuring the weight and time. Salt retentions are measured using 5 mM of NaCl, MgSO₄, MgCl₂, or Na₂SO₄ at an applied transmembrane pressure of 2 bars and a crossflow velocity of 1 m·s⁻¹ which corresponds to a Reynolds of 675, well within the laminar flow regime. Retention is determined by measuring the feed and permeate conductivity using a WTV conductivity meter, subsequently the retention is calculated using **Equation 7.2**. At least 20 ml of permeate is collected before the permeate conductivity is measured.

$$R = \frac{\Delta C}{C_{feed}} \cdot 100\% \quad (7.2)$$

MWCO is determined at the same conditions as the salt retention experiments and are performed by permeating a solution containing ethylene glycol (EG), diethylene glycol (DEG), and various molecular weights of poly(ethylene glycol) (PEG). The following molecular weight were used; EG62, DEG106, and PEG(200, 400, 600, 1000, 1500, and 2000 g·mol⁻¹). Of each molecule, 1 g·L⁻¹ is dissolved in demineralized water

7.3 Results and Discussion

The results and discussion section is split into two separate parts; first the fundamental layer buildup of proteopolymersome (PP+) multilayers (PPMs) and second their performance as separation layer. In the fundamental part, the layer buildup of the two PPMs will be studied by means of reflectometry and SEM images. In the membrane performance part, the permeability and MgSO_4 retention of the fabricated multilayers will be discussed as a function of the number of layers, while for both systems selected layers are also more thoroughly studied for their MWCO and more detailed salt retention (NaCl , MgCl_2 and Na_2SO_4). Throughout, the PPMs are compared to traditional PEMs. For this comparison three well studied PEMs are used; PAA/PAH, PSS/PAH, and PSS/PDADMAC based multilayers with the polyelectrolyte structures being shown in **Figure 7.1**. As discussed in the introduction, these PEMs are chosen because of the different interaction between weak and strong polyelectrolytes and the resulting membrane characteristics and performances. Finally, the results obtained in this study will be compared to literature results on aquaporin based membranes.

Figure 7.1: Polyelectrolytes used in this study in order to fabricate polyelectrolyte multilayers and proteopolymersome multilayers.

7.3.1 Multilayer characterization

To evaluate if multilayers can be fabricated using just PP+ and polyelectrolytes, optical fixed angle reflectometry was used to quantitatively characterize the PPM growth using PAA and PSS as the polyanion and PP+ as the positively charged species. Similar to other multilayer studies using reflectometry, the polyelectrolyte solutions and the PP+ solutions are flown perpendicular to the surface of the silicon wafer in an alternating fashion. The hydrodynamics in the flow cell are such that convection plays no role and that the adsorption is diffusion limited, just as in the dip-coating processes used to coat the membranes. [30] In **Figure 7.2**, the adsorption of PPMs in combination with PAA (left figure) and PSS (right figure) are plotted as function of the number of layers. Here, we observe a steady layer growth for both polyanions demonstrating that a multilayer can indeed be fabricated using PP+ as the positively charged species in combination with

either PAA or PSS as the polyanion. Using PAA as the polyanion, as shown in **Figure 7.2A**, it is observed that the relative growth of PP+ comparing to PAA is eight times larger, with an higher adsorption of $4 \text{ mg}\cdot\text{m}^{-2}$ for the last PP+ layer and just $0.5 \text{ mg}\cdot\text{m}^{-2}$ for the last PAA layer. Similar behavior is observed when PSS is used as the polyanion (**Figure 7.2B**), however, in a lesser amount with $2.5 \text{ mg}\cdot\text{m}^{-2}$ for the last PP+ layer and $1.8 \text{ mg}\cdot\text{m}^{-2}$ for the last PSS layer. This shows that that the total amount of mass of PP+ is in excess within the multilayer, indicating a high amount of PP+ inside of the layers. As an additional test, the fabrication of PPMs based on PP+ in combination with polycations was attempted. This resulted in unstable adsorption and no PPM layer growth, as expected based on the small positive charge of PP+. In summary, the incorporation of PP+ in multilayers is a relatively straightforward process in combination with the polyanions PSS and PAA.

Figure 7.2: Reflectometry results on the adsorption of PPMs as function of layer number. A: PAA is used as the polyanion and PP+ are used as the positively charged agent. B: PSS is used as the polyanion in combination with the positively charged PP+. Error bars are standard deviations of three separate measurements. When the error bars are not visible, the error is smaller than the data point symbols.

Subsequently, these PAA/PP+ and PSS/PP+ multilayers were fabricated on hollow fiber membrane supports and imaged by SEM. In **Figure 7.3**, PAA based PPMs are shown and no distinct polymersomes or vesicle shaped structures are observed on the active surface layer of the membrane. Moreover, the clear agglomeration of polymer material looks like

typical dewetting [31, 32] behavior where the polymer coatings are too mobile and do not wet the surface.

Figure 7.3: FE-SEM images of PAA/PP+ multilayers on top of a $[\text{PAA/PAH}]_1\text{PAA}$ multilayer. A: PPM terminated by PAA. B: PPM terminated by PP+. All multilayers were deposited on the inside of hollow fiber membrane supports.

For the PPMs in which PSS is used as the polyanion together with the PP+, the same procedure was followed at which the vesicles were constructed on top of a 1.5 bilayer thick $[\text{PSS/PAH}]_1\text{PSS}$ multilayer. In **Figure 7.4A and C**, solely the $[\text{PSS/PAH}]_1\text{PSS}$ and the $[\text{PSS/PAH}]_2$ multilayers without PP+ are imaged and a relative smooth surface can be seen. It is observed that the PSS terminated multilayer is smoother than the PAH terminated multilayer which is in accordance with roughness values reported in literature. [33] However, when having just a single layer of PP+ deposited on the surface, as shown in **Figure 7.4B**, it is observed that the surface roughness increases and that the surface is covered with small and larger components. Here, it is noticed that the smaller components outnumber the larger components. It is expected that the larger components are the proteopolymersomes since the size should be around >150 nm according to the dynamic light scattering (DLS) measurements as mentioned in the Materials and Methods section and the transmission electron microscopy image shown in **Figure S7.1**. However, the PP+ appear smaller than in the DLS measurement, most likely because they collapse during SEM imaging due to the high vacuum used. Nevertheless, vesicular shaped structures are clearly observed indicating that the PP+ are present on and in the active layer of the membrane for the PSS/PP+ PPMs.

It is important to check if the PPM is stable and that the PP+ are still present after membrane filtration test. In **Figure 7.4D**, the PP+ terminated surface is imaged after the membrane was exposed to membrane filtration tests. Here, it is seen that the small components are not observed on the surface anymore, although the larger PP+ (vesicular structures) components are still present on the surface. This shows that even after filtration, the PP+ are still present on the surface of the hollow fiber membrane. In **Figure 7.4D** the pore structure below the layers seems more visible than in **Figure 7.4C**. Still, molecular weight cut-off (MWCO) measurements with PP+ terminated multilayers show that these membranes do not contain any defects. These experiments will be more elaborately discussed in the next section.

Figure 7.4: FE-SEM images of $[\text{PSS}/\text{PAH}]_1\text{PSS}$ and the $[\text{PSS}/\text{PAH}]_2$ multilayers (A and C respectively) and PP+ terminated multilayers before and after filtration tests (B and D respectively). All multilayers were deposited on the inside of hollow fiber membrane supports.

7.3.2 Membrane performance

In this section the membrane performance of the PPMs will be assessed and compared to PEM membranes based on the same polyanions. The first multilayers tested are the PAA/PP+ and the PAA/PAH multilayers where both the permeability and retention results are plotted in **Figure 7.5A** and **B** respectively. The first three layers, [PAA/PAH]₁PAA of the PPM are the same as the PEM to obtain a good primer layer. It is observed that the PAA/PP+ multilayer (solid line) has a higher permeability after eight layers than the PAA/PAH multilayers (dashed line). The PAA/PP+ multilayer decreases the permeability steadily with more layers and eventually obtains a permeability of $2.6 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ whereas the PAA/PAH multilayers has a permeability of $0.6 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ after eleven layers. When looking at the MgSO_4 retention, however, it is observed that for the PAA/PP+ multilayer the retention stabilizes already after three layers, the point after the primer layer where the PAA/PP+ multilayer starts to build. The decreasing permeability in combination with the reflectometry results (**Figure 7.2**) suggests that a layer is built on the surface. However, the MgSO_4 retentions do not show an increasing trend as the control PAA/PAH multilayer does. This is indicative of a defective layer as suggested already by the SEM images in **Figure 7.3**. Furthermore, in **Figure 7.5C** together with the retention of MgSO_4 , NaCl, MgCl_2 , and Na_2SO_4 , the MWCO is shown for the 5 and 5.5 bilayer thick PEMs and PPMs, as indicated by the arrows in **Figure 7.5A** and **B**. Retention of various salts was measured in order to obtain more understanding about the rejection mechanisms of all the PPMs and PEMs build. In these figures, it is clearly seen that the PAA/PP+ PPM is defective regardless of the terminating layer in comparison to the defect-free PAA/PAH PEM, since the overall salt retention is very low in combination with a high MWCO of around 1 kDa. The PAA/PAH PEM membranes have a relatively high retention toward MgCl_2 and MgSO_4 indicating that a positive charge is most dominant within these PEMs, in combination with a low 250 Da MWCO.

Figure 7.5: Permeability (A) and MgSO₄ retention (B) of PAA/PP+ and PAA/PAH multilayers as function of the number of layers. Retention of various salts (C) for both PAA/PP+ and PAA/PAH multilayers having 5 and 5.5 bilayers respectively. Both permeability and retention measurements were performed at 2 bars of pressure and a crossflow velocity of 1 m·s⁻¹. The arrows indicate the membranes that are used for further salt retention and MWCO measurements. For the retention measurements a concentration of 5 mM was used. Error bars are standard deviations, n=5.

The second multilayer to study is the PSS/PAH PEM multilayer and the corresponding PAH/PSS/PP+ PPM multilayer. In **Figure 7.6A** (solid line), it is seen that the permeability decreases steadily when increasing the number of layers, in line with the reflectometry results. The first two layers are PEs and it is seen that a PSS/PP+ layer is neatly constructed after this point where the PSS/PP+ multilayer starts to be built. Compared to a PSS/PAH multilayer (dashed line), it is noticed that after the primer layer ($[\text{PSS/PAH}]_1\text{PSS}$) the PSS/PAH multilayer has a consistently higher permeability than the PSS/PP+ multilayer. The PSS/PP+ multilayer stabilizes at a permeability of $7.7 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ after eleven layers, whereas the PSS/PAH multilayer stabilizes at a much higher permeability of $12 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$, indicating that the PSS/PAH multilayer is less resistant to water and thus more permeable than the PSS/PP+ multilayer. This could be seen as surprising as aquaporin containing vesicles were able to increase the permeability of membranes prepared by interfacial polymerization [20]; why would a layer that contains mostly vesicle (see figure 2b) not have an improved permeability? Here it is important to realize that PEM coatings have such a high permeability especially due to low thickness of the coatings ($< 50 \text{ nm}$), while the vesicles themselves are much larger in size ($150\text{--}200 \text{ nm}$). This discrepancy in layer thickness is likely why the PEM outperforms the PPM in terms of permeability.

When looking at the retention of MgSO_4 as function of the layer number, shown in **Figure 7.6B**, the transitioning from the pore-dominating to the layer-dominating regime can be nicely observed. This transition starts after 4 layers and it is the point at which the multilayer is starting to form a layer on top of the pores instead of a layer on the wall of the pores. [34] After the complete transition from the pore-dominating to the layer-dominating regime after 7 layers, it is noticed that the PSS/PAH multilayer stabilizes at a MgSO_4 retention of 94% and the PSS/PP+ multilayer at a retention of 80%. When comparing the retention toward various salts for both multilayers as shown in **Figure 7.6C**, it is observed that the retention toward NaCl and MgSO_4 is slightly higher for the PEM membrane than the PPM membrane. Moreover, a strong effect is seen whether the PSS/PAH multilayer is PSS or PAH terminated with a higher NaCl retention for the PAH terminated multilayer and a high Na_2SO_4 retention for the PSS terminated multilayer. When comparing the MgCl_2 and Na_2SO_4 retentions of the PSS/PP+ and PSS/PAH multilayers, Donnan-exclusion is seen for the PSS/PAH membranes, showing a high removal of positive charged ions and lower for negative species due to an excess of PAH within the multilayer. [25] The opposite can be observed for the PSS/PP+ layers which show a high Na_2SO_4 retention but low MgCl_2 retention meaning that within the

PSS/PP+ layers a negative charge is dominant due to the high charge density of PSS. This means that by using PP+ instead of PAH, the charge balance of the multilayer can be altered and a predominantly negatively charged multilayer can be obtained. This is likely due to the much lower charge density of the PP+ in comparison to PAH, and therefore, the negative charge of PSS becomes dominant.

Figure 7.6: Permeability (A) and MgSO₄ retention (B) of PSS/PP+ and PSS/PAH multilayers as function of the number of layers. Retention of various salts (C) for both PAH/PSS/PP+ and PSS/PAH multilayers having 5 and 5.5 bilayers respectively. Both permeability and retention measurements were performed at 2 bars of pressure and a crossflow velocity of 1 m·s⁻¹. The arrows indicate the membranes that are used for further salt retention and MWCO measurements. For the retention measurements a concentration of 5 mM was used. Error bars are standard deviations, n=5.

The third and last multilayer studied is the PSS/PDADMAC PEM and PDADMAC/PSS/PP+ PPM. In essence the PDADMAC/PSS/PP+ and PAH/PSS/PP+ are the same PPM based on PP+ and PSS, however, both are constructed on a different primer layer of [PAH/PSS]_nPAH and [PDADMAC/PSS]_nPDADMAC respectively. The main difference between the other two PEMs studied in this article is that PSS/PDADMAC is completely build using strong PEs, whereas PSS/PAH has one weak PE and PAA/PAH two weak PEs. In **Figure 7.7A** and **B**, the permeability and MgSO₄ retention are plotted as function of the number of layers for PSS/PP+ and PSS/PDADMAC multilayers. Here, the permeability shows a steady decrease for the PSS/PP+ multilayer after the primer layer and stabilizes at $3.5 \pm 1.2 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ after eleven layers. This shows that a PPM is built on top of the surface of the hollow fiber support membrane. The PSS/PDADMAC multilayer shows a strong odd–even effect [35] and on average has a higher permeability with increasing layer number of 7.2 ± 1.1 and $5.4 \pm 1.2 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ for PDADMAC and PSS terminated PEMs with thicknesses of 5 and 5.5 bilayers respectively. MgSO₄ retentions stabilize at $88\% \pm 2\%$ to $89\% \pm 1\%$ depending on the terminated layer for the PSS/PDADMAC multilayer and stabilize at around $84\% \pm 7\%$ for the PDADMAC/PSS/PP+ multilayer. When looking at **Figure 7.7B**, the retention for MgSO₄ stabilizes around the same value within the error margins for both the PSS/PDADMAC and PDADMAC/PSS/PP+ layers, meaning that both multilayers perform equally.

The retention of various salts is for the PDADMAC/PSS and PDADMAC/PSS/PP+ multilayers having 5 and 5.5 bilayers (indicated by the arrows in **Figure 7.7A** and **B**) is plotted in **Figure 7.7C**. Here, the retention of NaCl in **Figure 7.7C** shows a strong odd–even effect when the PEM is terminated on either PDADMAC or PSS. The NaCl retention is highest when the multilayer is PDADMAC terminated due to the high amount of positive charge. [36] This is also observed for the high MgCl₂ retention and the subsequent low Na₂SO₄ retention for a PDADMAC terminated PEM. When the PSS/PDADMAC PEM is PSS terminated, the NaCl retention is low (around 10%) and an opposite Donnan–exclusion effect is observed due to the high Na₂SO₄ retention and relatively low MgCl₂ retention. The same Donnan–exclusion can be seen for the PPMs independent of the terminated layer, indicating that the PPM contains a lot of negative charge. The same was seen for the PAH/PSS/PP+ PPM, most likely due to PSS dominating the charge balance within the PPM, whereas PDADMAC is dominating the charge within the PEM. [37] The same conclusion holds for PSS/PAH multilayers, that PP+ has a lower charge density than PDADMAC, and for this reason, when PP+ is used the charge balance can be changed resulting in negatively charged multilayers.

Figure 7: Permeability (A) and MgSO₄ retention (B) of PSS/PP+ and PSS/PDADMAC multilayers as function of the number of layers. Retention of various salts (C) for both PDADMAC/PSS/PP+ and PSS/PDADMAC multilayers having 5 and 5.5 bilayers respectively. Both permeability and retention measurements were performed at 2 bars of pressure and a crossflow velocity of 1 m·s⁻¹. The arrows indicate the membranes that are used for further salt retention and MWCO measurements. For the retention measurements a concentration of 5 mM was used. Error bars are standard deviations, n=5.

7.3.3 Literature comparison

In the previous sections it was shown that defect-free PPMs can be fabricated using PSS as a polyanion and PP+ as the positively charged species creating a PAH/PSS/PP+ and a PDADMAC/PSS/PP+ multilayer membrane. The PPM based membranes show very relevant performance as NF membranes and it was shown that although the PPMs did not outperform the PEMs, the charge of the multilayer could be changed. When using PP+ instead of a polycation, the overall charge of the multilayer can be altered to negative instead of positive. In this section of the article, the PPMs fabricated in this study will be compared to aquaporin containing proteoliposome or proteopolymersome based membranes reported in literature.

In **Table 7.1**, the permeability, salt retentions, and fabrication methods of membranes fabricated in this study and values reported for aquaporin based membranes (ABMs) in literature are summarized. In literature various approaches were used in order to incorporate the vesicles. Here, most studies fixed proteoliposomes using interfacial polymerization (IP) (ABM1 [20], ABM2 [25], ABM3 [43], ABM4 [22], ABM5 [44], and ABM6 [45]). Other approaches incorporating vesicles include fixating proteoliposomes using PE crosslinking (ABM7) [46], surface imprinting polymerization with proteopolymersome (ABM8) [47], and embedding proteoliposomes into a layer-by-layer assembled membrane (ABM9) [24]. Studies fabricating supported lipid bilayers used techniques to fuse proteoliposomes on existing membranes in order to construct a supported lipid bilayer (SLB) membrane (ABM10) [48], rupture and crosslinking of proteoliposomes on a polydopamine support layer (ABM11) [49], and ruptured proteoliposomes on top of a PEM membrane (ABM12) [50].

ABM1 till 6 are membranes that incorporated proteoliposomes using IP, these membranes generally have a high NaCl retention, typical for IP based membranes. For this reason, these membranes outperform the PPM and PEM membranes fabricated in this study in terms of salt rejections. Only the MgCl₂ retention was measured for ABM7, 8, and 9 that were constructed using different incorporation methods. Here it can be observed that the membrane performance depends hugely on the incorporation approach where, e.g., high permeabilities of 36.6 L·m⁻²·h⁻¹·bar⁻¹ and 85% MgCl₂ retention were measured for ABM7. Whereas for ABM8, also a high permeability of 23 L·m⁻²·h⁻¹·bar⁻¹ was measured but a much lower MgCl₂ retention of 51%. ABM9 has a permeability of 6 L·m⁻²·h⁻¹·bar⁻¹, a MgCl₂ retention of 95%, and uses PAH and PSS-PAA to incorporate proteoliposomes in the active layer using flat sheet PAN supports. In our study, the preparation method is different where PP+ are used and a multilayer is built by alternately adsorbing PP+ and

polyanions, while in the study of Sun et al. [24], only one layer of proteoliposomes was adsorbed into the PE layer. The PAH/PSS/PP+ membranes in this study have a higher permeability of $8.7 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ in comparison to ABM9 but a lower MgCl_2 retention of 50-60% due to the negatively charged nature of this PPM. For the SLB membranes (ABM10, 11, and 12) there is quite a large spread in performance where ABM11 and 12 perform well with MgCl_2 retentions of 90% and 97%. However, ABM10 only has a NaCl retention of 20% indicating that such layers are quickly prone to form defects. Comparing the retention of all membranes is a difficult task since it depends on many factors, among others, the surface charge and type of salt retention measured. The studies in literature mostly report the retention of just one type of salt. For example, for ABM7, 8, 9, 11, and 12 only the retention for MgCl_2 was measured, when the membranes have a strong positive charge, MgCl_2 retention will be high. To compare it to this study, the retention for Na_2SO_4 for PAH/PSS/PP+ and PDADMAC/PSS/PP+ membranes fabricated is very high with values of 85-90% due to the dominant negative charge of the membranes giving especially high retention toward negative divalent ions instead of positive divalent ions. Such a diversity in retention behavior adds to the scope of possible applications for PEM and PP+ based membranes.

Table 7.1: Summarized values for permeability, salt retentions, and incorporation methods for aquaporin based membranes (ABMs) in this work and literature and PEM membranes in this study.

Membrane type	Incorporation approach	Permeability ($\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$)	Salt concentration	Salt retention
Polyelectrolyte multi-layer (PEM)				
[PSS/PDADMAC] ₅ PSS	N.A.	5.4	5 mM	9% NaCl, 67% MgCl ₂ 90% Na ₂ SO ₄ , 89% MgSO ₄
[PSS/PAH] ₅ PSS	N.A.	12.3	5 mM	26% NaCl, 96% MgCl ₂ 80% Na ₂ SO ₄ , 94% MgSO ₄
[PAA/PAH] ₅ PAA	N.A.	2.6	5 mM	9% NaCl, 57% MgCl ₂ 34% Na ₂ SO ₄ , 60% MgSO ₄
Proteopolymersome multilayer (PPM)				
PDADMAC[PSS/PP+] ₄ PSS	LbL ^a	3.5	5 mM	8% NaCl, 48% MgCl ₂ 90% Na ₂ SO ₄ , 84% MgSO ₄
PAH[PSS/PP+] ₄ PSS	LbL ^a	7.7	5 mM	11% NaCl, 54% MgCl ₂ 85% Na ₂ SO ₄ , 80% MgSO ₄
PAH[PAA/PP+] ₄ PAA	LbL ^a	0.6	5 mM	8% NaCl, 17% MgCl ₂ 1.0% Na ₂ SO ₄ , 10% MgSO ₄
Literature values				
ABM1 [20]	IP ^b	4.0	10 mM	97% NaCl
ABM2 [25]	IP ^b	8.0	500 ppm	97.5% NaCl
ABM3 [43]	IP ^b	3.2	1000 ppm	69.6% MgSO ₄ , 16.5% NaCl
ABM4 [22]	IP ^b	6.4	500 ppm	93.5% NaCl
ABM5 [44]	IP ^b	1.3	2000 mg/L	99.1% NaCl
ABM6 [45]	IP ^b	2.4	2000 ppm	99.6% NaCl
ABM5 [46]	CL ^c	36.6	100 ppm	85% MgCl ₂
ABM6 [47]	Pol ^d	23	200 ppm	51% MgCl ₂
ABM7 [24]	LbL ^a	6.0	200 ppm	95% MgCl ₂
ABM8 [48]	SLB ^e	4.8	1 mM	20% NaCl

^a: Layer-by-layer assembly. ^b: Interfacial polymerization. ^c: Crosslinking. ^d: Polymerization. ^e: Supported lipid bilayer

7.4 Conclusions

In this study, we show that the incorporation of aquaporin containing proteopolymersomes in PEM films is a simple and straightforward procedure. It is shown by reflectometry that a multilayer can be built using a polyanion and PMOXA-PDMS-PMOXA based proteopolymersomes (PP+) as the positively charged species. When the two are deposited alternately, a PP+ multilayer (PPM) is fabricated, here shown for both PAA/PP+ and PSS/PP+. These multilayers can simply be constructed on the inside of hollow fiber ultrafiltration supports to form PPM based nanofiltration (NF) membranes. By SEM it is shown that PP+ are present in the PSS based PPMs but form a dewetted structure for the PAA based PPMs. When comparing the membrane performance of the PPMs, it is seen that the PAA based PPM membranes contain defects, while the PSS based PPM forms a good membrane with 80-83% MgSO_4 retention. MWCO measurements (< 350 Dalton) further demonstrate that the PSS based PPM membranes form very relevant NF membranes. In comparison to PEM membranes (PAA/PAH, PSS/PAH, and PSS/PDADMAC), no performance increase in either selectivity or permeability is observed. However, dominant negatively charged layers could be formed when using PPMs instead of the dominant positively charged PEMs. This is most likely due to the relative low charge density of the PP+ in comparison to PSS. When the PPM membranes are compared to literature, IP based aquaporin containing membranes outperform the membranes in this study based on salt rejection. However, our membranes showed similar performances in terms of permeability and retention with non IP based aquaporin based membranes, while being more optimized towards the retention of divalent anions. In summary, this study provides fundamental understanding on the buildup of PPM membranes and the resulting membrane performances and shows that well performing hollow fiber based PPM membranes can be fabricated by a very simple approach.

7.5 Acknowledgements

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7.6 Supplementary information

7.6.1 Transmission electron microscopy

Figure S7.1: Transmission electron microscope image of a PP+ sample.

7.7 References

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Chapter 8

Outlook

*“If all you do is coast, eventually you slow down,
while others catch up and pass you by.”*

Neil deGrasse Tyson – US senate testimony 2012

Astrophysicist, cosmologist, and science communicator

From the beginning through to the end of this thesis, polyelectrolyte multilayers (PEMs) have been tuned, optimized, modified, and post treated in order to make them denser and to control their separation properties. The overarching aim was to create denser PEM membranes to allow them to be applied in RO and FO processes, but also to understand how PEM material properties influence eventual performance in membrane applications.

Chapter 2 shows that polycation excess in PDADMAC/PSS based membranes, influences final membrane performance in a way that can no longer be controlled by simply terminating the layer with a negatively charged polyelectrolyte. Using salt annealing, a simple post-treatment step, membrane surface charge can be manipulated again and this directly translates into control over the membrane separation properties. **Chapter 3**, also uses a post treatment step, but now to control the hydration or swelling degree of the PEM membrane. Here, the very hydrophobic polyelectrolyte called Nafion is used to decrease the amount of water inside the multilayer. The resultant decrease in hydration when Nafion is used results in a denser multilayer which is able to reject organic contaminants to a much higher degree. For the more conventional polyamide based TFC membranes, the density of the separating layer is known to strongly influence both the MWCO and the salt retention. With the developed Nafion multilayer in this study, the salt retention is unchanged while the MWCO is decreased meaning that the salt retention and MWCO can be decoupled. This effect is stronger when a Nafion based multilayer is built on top of the existing PEM creating an asymmetrical PEM.

In **Chapter 4** this decoupling of salt and organic molecule retention is taken a step further. Here two different PEMs are combined; one that has an open structure to ensure pore closure and one with a dense structure to act as the selective top layer to block organic molecules. Using this approach, a membrane with a high permeability, high organic molecule retentions, and low salt retentions is obtained. These unique membrane properties are only possible because of the asymmetric layer buildup. The asymmetric layer buildup allows a thin selective layer of only 4 nm to be on top and determining the main separation while keeping permeabilities high. This extreme form of asymmetry is very much in line with the philosophy of Loeb-Sourirajan when they developed asymmetrical cellulose acetate RO membranes. [1] Due to the asymmetrical structure of their RO membrane, energy costs decreased significantly making desalination a viable option. This very development can be seen as the start of modern membrane technology.

Chapters 5 and 6 describe different PEM membranes to study the role of the polycation and the crosslinkability in both nanofiltration and forward osmosis processes. In **Chapter 5**, the material properties of the PEMs are thoroughly studied in combination

with a complete nanofiltration study. This highlights the clear connection between PEM material and separation properties. Subsequently, in **Chapter 6** the same membranes are tested in forward osmosis processes showing that when combined with the right type of draw solution, low reverse salt fluxes can be obtained. However, when retaining various charged micropollutants, Donnan dialysis can occur with ionic draw solutions that has a monovalent ion and a multivalent counterion leading to low or even negative retentions.

In **Chapter 7**, an entirely different approach is taken where the polycation is exchanged by aquaporin containing proteopolymersomes and instead of making a PEM, a proteopolymersome multilayer (PPM) is fabricated. The aquaporin in the proteopolymersomes is highly selective and permeable for water giving it the potential to boost membrane performance. Using this approach very relevant NF membranes can be fabricated and the charge balance within the multilayer can be changed from positive for the studied PEMs to negative for the PPMs. Since the charge density of the proteopolymersomes is low in comparison to the polyanion, the charge of the polyanion dominates the multilayer. Apart from changing the charge of the multilayer, no water permeability nor retention improvements were observed when compared to PEM membranes. The reason why no improvement was observed is most likely because the PEM in which the proteopolymersome are embedded is too permeable. In this case, the majority of water permeates through the polyelectrolyte layer and is not forced through the aquaporin proteins not allowing the proteins the chance to demonstrate their selective nature.

In the next sections an outlook and a future perspective is presented; discussing how the field of PEM membranes should progress based on the knowledge obtained in this thesis as summarized above. Various ideas are proposed to improve PEM membrane performance, gain more knowledge, and to conduct research more thoroughly specific for PEM membranes.

8.1 Annealing as a post treatment step for every type of polyelectrolyte multilayer

In this section, the obtained annealing results from **Chapter 2** are placed into a larger perspective in order to show future ideas for this subject. PEMs are known to be kinetically trapped systems [2] and using annealing approaches such as the one described in **Chapter 2**, an increase in performance and most likely stability can be obtained. Firstly,

after an annealing step the PEM has equilibrated [3] due to the increased interdiffusion of the PEs within the layers. [4] An equilibrated PEM will be more stable when it is operated in membrane processes: since the PEM is not equilibrating over time anymore, no changes in membrane performance are expected over time. Annealing with a subsequent adsorption step of the oppositely charged PE might result in more stoichiometric layers potentially increasing the amount of ionic crosslinks. [5] Annealing of PSS/PDADMAC has been extensively studied, however, its use in other PEMs especially PEMs containing weak PEs has not been thoroughly studied yet.

Studies have attempted to use annealing in order to improve PEM membrane performance having weak PEM systems like PAA/PAH. [6] However, the problem is that the exact annealing conditions are specific for each PEM system and need to be understood in order to make annealing an effective post treatment. For PSS/PDADMAC multilayers it is known that they undergo a glass transition at a salt concentration above 1.0 M of NaCl. [7] However, for other systems this can be entirely different, for example; PSS/PAH multilayers show a stable thickness up to 2 M of NaCl meaning that these multilayers can still be considered as glassy at those salt concentrations. [8] On the contrary, PAA/PAH multilayers are known to be very mobile, resulting in unstable adsorption when the salt concentration exceeds 0.5 M of NaCl. [9] This already shows key differences for these PEMs, namely the stability order for these PEMs is; PSS/PAH > PSS/PDADMAC > PAA/PAH. For these differences in mobility, the annealing condition should be chosen correctly in order to achieve the desired effect.

In addition, when the aim is to create a stoichiometric multilayer, annealing should always be paired with a subsequent adsorption step of the oppositely charged PE. When one of the PEs is weak, salt annealing in combination with a pH that charges the weak PE can help to make the annealing process more effective. [10] A subsequent adsorption step ensures a higher adsorption of the oppositely charged PE that compensates the excess of one charge. Furthermore, this approach gives additional control over the surface and bulk charge of the PEM regardless of the type of PEs used and the possibility to create more stoichiometric multilayers.

8.2 Crosslinking for enhanced selectivity

Continuing on the concept of crosslinking that was explored in **Chapters 5** and **6**, three different approaches can be used; the layer can be made positively or negatively charged

by removing one charge by crosslinking, for example the Schiff base reaction between amine and aldehydes, [11] in order to increase ion retentions; secondly, all charges are removed, in this way the layer could possibly be made so dense that the layer is able to exclude all ions from solution due to size exclusion; and thirdly by crosslinking but no charges are removed (e.g. alternating block-co-polymers with crosslinking groups). By using crosslinking, the swelling degree of the PEM is lowered and when the charges of the PEs are still present this can result in a higher effective charge density. However, when only one charge is removed the multilayer becomes denser while decreasing its charge density. When all charges of the PEs are removed, the PEM can be made even denser since the charges are not repelling each other anymore allowing for a denser packing.

Two ways can be used to fabricate crosslinked multilayers namely post covalent conversion and consecutive covalent fabrication. [11] The first means that crosslinking happens after the entire PEM is built and the second approach uses crosslinking after each adsorption step. From a practical perspective one would prefer to crosslink only once, after the PEM is built, therefore it can be as simple as a single post treatment step.

Different crosslink chemistries can be used in order to make a PEM denser, in literature the most commonly used crosslinking agent for PEMs is glutaraldehyde (also used in this thesis). Using a crosslinking agent like glutaraldehyde makes the crosslinking process easy since the membrane only has to be dipped inside a solution containing the agent. However, when using a crosslinking agent to make an already dense multilayer denser, only small crosslinking agents can be used that can permeate the multilayer while it is densifying. Glutaraldehyde, glyoxal, and small diepoxides are very small, but these chemistries are harsh and the chemicals can be very harmful. For this reason, the usage of these crosslinking agents is difficult in a commercial application, and therefore, other types of crosslinking chemistries should preferably be used.

The dialdehyde and diepoxide molecules react with the amines in the PEM structure and remove the positive charges from the PEM. The second approach is to remove all the charges within the PEM. For the PAA/PAH multilayer, the amines can react with the carboxylic acids to form amide bonds [12] and this amidization can be simply performed by heating the multilayer between 130-270°C for 1-2 hours. [13-16] However, the problem with nanofiltration PEM membranes is that the ultrafiltration support becomes dry during the process and results in pore collapse that causes the membrane to become impermeable. This could be avoided by keeping the support wet by pressurizing the outside (shell) side with water while flowing hot air through the inside (lumen) side of the fibers where the PEM is located.

8.3 Further improving asymmetrical PEM membranes

Since a crosslinking post-treatment step is desired from a fabrication point of view, asymmetric membranes as shown in **Chapter 3** and **4** are ideal candidates for this approach. Only the thin top layer has to be crosslinked meaning that the crosslinking agent like glutaraldehyde does not need to penetrate the entire multilayer. For the asymmetric PSS/PAH – PAA/PAH membrane, amidization by heat like discussed in the previous section can be a perfect way to create an even denser top layer. However, crosslinking can cause stress, especially in these very thin top layered PEMs, resulting in defects. Here, the asymmetrical approach prevents defects from dominating due to the bottom layer acting as a gutter layer like in membranes used for gas separation.

Using aromatic PE structures that are bulkier can lead to a faster growth of the PEM meaning that the layer-dominated regime is reached earlier. Aromaticity can be increased on the polycation side and by using PEs like poly(4-amino styrene) (PAS) and poly(vinyl benzyl trimethyl ammonium chloride) (PVBAC) shown in **Figure 8.1**. In addition, aromatic PEs like poly(4-aminostyrene) showed very high permeabilities of $22.2 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ for a 10 bilayer PSS/PAS system. This was discussed in Chapter 4 and shows that aromatic systems can most likely make the asymmetrical PEMs more permeable. Furthermore, when quaternary amines are used, the chemical stability of the composite PEM can be increased. A PE like PVBAC is both aromatic and has a quaternary amine that increases the chemical resistance of the PEM. Moreover, a 10 bilayer system of PSS/PVBAC was tested and had permeabilities of $25.5 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ even higher than the PSS/PAS multilayer. This already shows the possibility of increasing both the permeability and chemical stability of asymmetrical PEMs by increasing the aromaticity.

As mentioned in the previous paragraph, chemical stability toward cleaning agents like hypochlorite is very important for asymmetrical PEM membranes in order to make the next step to commercial membranes. In the ideal case, both the bottom and top layer of the asymmetric PEM membrane would be chemically stable. However, this is difficult to achieve both since the most selective structures are usually prone to degradation, like the amide bonds created by amidization. It is important to start making the bottom layer chemical resistant since the most layers are needed here. It would be best if a crosslinking chemistry can be found to make the top layer chemically stable, however, if only the thin top layer deteriorates it is quite a simple operation to sacrifice [9] and to reapply the top coating again due to the limited amount of layers, without reapplying the bottom coating.

Figure 8.1: Aromatic polycations; poly(4-amino styrene) (PAS) on the left containing a primary amine; and poly(vinyl benzyl trimethyl ammonium chloride) (PVBAC) on the right that has a quaternary amine.

8.4 Perfluorinated polymers for low hydrated polyelectrolyte multilayers

If a PEM with low hydration is the goal, simpler processing steps can be taken since crosslinking is not the only approach available. An application of just a final layer of Nafion is easy, results in low hydration and is quickly deposited from ethanol containing solutions like shown in **Chapter 3**. Nafion is a perfluorinated polymer with a sulfonated group on the branched side chain. The hypothesis of **Chapter 3** is that Nafion is penetrating the multilayer and this results in dehydration of the layer. When a PE penetrates the multilayer, the kinetics and thus the magnitude of the dehydration likely depends partly on the mobility of the perfluorinated PE. For this reason, it would be interesting to study different types of perfluorinated polymers having different polymer structures. In **Figure 8.2A**, various structures of perfluorinated commercially available polymers are displayed with different side chain lengths.

Figure 8.2A: Various perfluorinated sulfonated polymers differing in chain length. B: Hypothetical relation between the charge density and mobility of the perfluorinated polymers and the PEM membrane selectivity (black solid line) and PEM hydration (red dashed line).

Nafion is the polymer used in this thesis, however, perfluorinated polymers having shorter side chains like the 3M™ and Aquivion®, [17] should have a higher mobility. In addition, 3M™ and Aquivion® do not have a methyl branch like Nafion®, this should result in higher penetration within the multilayer. Furthermore, when the side chain or overall backbone of the polymer becomes smaller, the charge density increases. With an increased charge density and higher mobility of the polymer, a relationship likely exists between the amount

of dehydration of the total PEM and the charge density/mobility, like suggested in **Figure 8.2B**.

Until now, the concept was to terminate the multilayer with a perfluorinated polymer like Nafion. However, the idea can be taken a step further where these perfluorinated polymers are used to construct complete multilayers. [18] When complete multilayers are constructed, the relation described in Figure B might become more dramatic resulting in denser and more selective PEMs with increasing charge density [19] of the perfluorinated polymers.

8.5 Use of Aquaporin containing vesicle in polyelectrolyte multilayer membranes

In this thesis, in **Chapter 7**, aquaporin functionalized polymersomes were used as the positively charged species to construct proteopolymersome multilayers (PPMs) in combination with a polyanion. Although the aquaporin protein is highly permeable and selective toward water and very relevant PPM membranes were fabricated, PEM membranes still have either a higher water permeability or selectivity than the PPM membranes. One of the likely reasons for this is that water is not forced through the protein since the PEM surrounding the proteopolymersomes is too permeable, meaning that the majority of water is permeating through the PEM. The other reason is that the use of proteopolymersomes decreased the total charge density of the multilayer that also results in lower retentions. Furthermore, the fit in a PEM is not ideal since PEMs have thicknesses of 20-50 nm where the proteopolymersomes have a diameter of around 120 nm. For this reason, the only way to fabricate aquaporin containing PEM membranes that benefit from the selective protein is to go for the asymmetrical approach.

The asymmetrical approach means that a PEM is present as the bottom layer, filling the support structure, and on top a thin layer containing the aquaporin proteins. Although these layers are prone to defects, [20] Werber et al. already theoretically described that when such a layer is put on top of polyamide based RO membranes, selectivity can increase. [21] The main factor that these layers could work is that the RO layer underneath acts as a gutter layer, the same can possibly be achieved by using a PEM. The proteopolymersomes could be ruptured [22] to create a thin biomimetic top layer on top of the PEM creating an asymmetrical PEM biomimetic membrane. In this manner, the

major part of water will be flowing through the aquaporin proteins increasing the selectivity of the PEM membrane.

8.6 Polyelectrolyte multilayer membranes for forward osmosis

It was found in this thesis that FO is possible with low reverse salt fluxes and high water fluxes by using PEM membranes in combination with the right draw solution. In **Chapter 6**, draw solutions were used that comprised of electrolytes and good results were obtained with PSS/PEI PEM membrane in combination with a trisodium citrate draw solution that contains a multivalent anion. Moreover, it was also shown that PEM membranes did not perform well when NaCl draw solutions were used, and therefore, do not outperform the existing polyamide based FO membranes. However, other chapters in this thesis show that the retention of salt and organic molecules can be decoupled and that PEM membranes are very good in retaining small organic solutes. For this reason, non-electrolyte draw solutions could hold the key for even higher performance in FO especially when retaining organic pollutants from the feed stream is of importance. These draw solutions could be as simple as sucrose, however, to maintain a high water flux the viscosity should not become too high. Other promising draws for PEM membranes could be the use of liquid-liquid phase separation of block copolymers or glycol ethers. [23] Since PEM membranes show high water fluxes combined with high retentions towards organic molecules, the right combination of draw and PEM could result in very well performing systems.

Moreover, it was shown that by retaining micropollutants, Donnan-dialysis occurred where selectively one micropollutant could be exchanged by sodium present in the draw solution. To prevent this from happening, it was found that by changing the draw solution to an organic draw like sucrose, selective permeation of charged species is stopped. On the other hand, this finding is interesting and could mean that charged species can be selectively removed by careful choice of the draw solution. In this case atenolol, a positively charged micropollutant, was exchanged by sodium over the negatively charge PSS/PEI membrane. Negatively charged micropollutants could therefore also be exchanged when the positively charged PSS/PAH membrane is used with a MgCl_2 draw. For this reason, this technique could be used for the separation of mixture containing charged and neutral

molecules, like for example amino acid mixtures, and should therefore be studied more thoroughly.

8.7 Simple methodology for studying polyelectrolyte multilayer membrane systems

In the previous sections ideas and hypotheses are given for further research and improvements on PEM based membranes. In this section, however, a simple methodology for conducting PEM membrane research is discussed to ensure a better research quality. With this methodology, every study conducted contributes to the very least a basic understanding of PEM structure and its influence on membrane performance (i.e. PEM defects, dominant charge, exclusion mechanism etc). In this thesis I showed that besides coupling the reflectometry growth curve to the resistance (inverse of the permeability) growth curve, [24] the MgSO_4 retention growth curve can also be coupled to the reflectometry growth curve (**Chapter 7**). Here a phase shift between the resistance and retention curves was observed, as shown in **Chapter 7**, and as illustrated in **Figure 8.3**.

Figure 8.3: Average expected resistance (black line) and MgSO_4 retention (red line) as function of the number of layers for a certain PEM membrane.

Following the black line in **Figure 8.3** indicating the resistance as function of the number of layers, a S-shaped curve can be seen where the layer-dominating regime starts at the

black dotted line. At this point the PEM on top of the support is dominating the membrane resistance, however, the PEM still contains defects. This is shown by the red line that represents the MgSO_4 retention as function of the number of layers. There is a phase shift between the start of the layer dominated regime indicated by resistance (black dotted line) and retention (red dotted line). For this reason, a third regime termed the defect dominated regime is proposed and this indicates the transition region until the PEM is entirely defect free. This also shows the importance of constructing both curves, since the shape of the curve depends on the PEM, the support, the coating conditions, and the deposition method. Constructing both curves will give a complete understanding how many layers must be coated in order to be in the layer dominated regime, and therefore, how many layers are needed to prevent defects that reduce membrane performance.

Besides the resistance and MgSO_4 growth curve, Na_2SO_4 and MgCl_2 (or equivalents salts) retentions should also be measured. There is a lot of literature that, for example, only measures MgCl_2 or another type of salt. These retentions can be very high only because of Donnan-exclusion since the PEM has either a dominant negative or positive charge. For this reason, at least one divalent cation and one divalent anion should be measured to provide insight into the charge of the PEM membrane, and therefore, its exclusion mechanisms.

8.8 Overall conclusion

In the beginning of this thesis the aim was to create the densest possible PEM membranes in order to function for RO and FO applications. However, a PEM membrane that can retain high amounts of NaCl , and therefore, compete with the existing polyamide based RO and FO membranes is not fabricated. In our opinion, PEM based membranes should not be seen as a direct competitor of the now commonly used polyamide based RO type membranes. Rather they represent new unique separation opportunities that will make new membrane separations and processes possible. In this thesis, a great deal of understanding, unique PEM membranes, and full control over every PEM membrane property is achieved. From controlling membrane charge with annealing, crosslinking, aquaporin containing proteopolymersomes, and different PEs; hydration with Nafion and crosslinking; and the decoupling of salt and organic molecule fluxes by asymmetry, and the use of either hydraulic or osmotic driving forces. This thesis shows the complexity of PEMs for membrane applications and the unique separations they offer the field.

8.9 References

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Summary

This thesis presents and discusses a variety of novel methods to control, manipulate, and modify the properties of polyelectrolyte multilayers (PEMs) for membrane applications. PEMs are thin polymer coatings, usually in the order of 5–50 nm, that are comprised of charged polymers called polyelectrolytes (PEs). Using the layer-by-layer (LbL) method, polyanions (negatively charged PEs) and polycations (positively charged PEs) can be alternately adsorbed onto any charged surface independent of geometry. The LbL approach is simple, whereby the desired substrate (e.g. a support membrane) is simply immersed in an aqueous solution containing a small amount of PE (~0.1 g/L) and some salt (0–0.5 M). After the first PE layer is deposited onto the substrate, the sample is rinsed and then immersed into a second aqueous solution containing the oppositely charged PE. In this manner, a desired number of layers can be built/prepared with precise control over the final thickness of the PEM. Furthermore, LbL deposition of PEs is a very versatile approach, allowing for control over not only the thickness, but also over the charge and density of the PEM, simply through changes in salt concentration, pH, and types of polyelectrolyte used. Throughout this thesis, PEM density refers to the packing density of the polyelectrolytes within the multilayer and swelling of the multilayer. The density in essence can be thought of the intrinsic pore size of the PEM – a denser PEM will have a lower pore size and will result in a higher resistance to water transport. PEMs that have a higher swelling will be more hydrated and will therefore have a lower density as opposed to PEMs that swell less. Due to its versatility and simplicity, the LbL method is very suitable for preparing novel membrane materials since PEMs can be easily coated on the inside of hollow fiber membranes, creating so-called hollow fiber PEM nanofiltration (NF) membranes. Access to the hollow fiber membrane geometry is highly advantageous, mainly because they have a smaller aspect ratio as well as lower fouling potential (no need for spacers) in comparison to flat sheet membranes.

The overarching aim of this thesis was to control the separation properties of PEM membranes and to create denser PEMs for increased membrane selectivities. The entirety of this thesis is based on varying the contents of the deposition solutions from which the PEMs are built, in order to increase the density and selectivity of PEM separation layers. A popular and well-studied PE pairing used in the fabrication of PEM membranes is that of the polycation poly(diallyldimethylammonium chloride) (PDADMAC) with the

polyanion poly(sodium 4-styrenesulfonate) (PSS). This PE pairing is so highly studied because it results in membranes with good separation properties and excellent chemical and physical stability. This high stability means that these PEM membranes can be cleaned without harming or degrading the active separation layer (i.e. the PEM layer) of the membrane. However, in such multilayers, PDADMAC is typically in excess and it is shown in **Chapter 2** that this non-stoichiometry within the PEM means that control over membrane surface charge and thus membrane separation properties is lost. This results in significant drops in sulfate retentions from 94% to 39%, indicating an increase in positive surface and bulk charge. In **Chapter 2**, it is shown for the first time on PEM membranes, that salt annealing can play an important role as a post-treatment step to regain control over the surface charge of such PEMs and thus over the separation properties of the membranes. Salt annealing just before the final PSS deposition step overcomes this PE excess problem and results in membranes with sulfate retentions of up to 97% and an even higher water permeability than multilayers membranes where no excess of PDADMAC is observed.

In the previous paragraph, a post-treatment step was performed in order to regain control over membrane surface charge. While in **Chapter 3**, an alternative post-treatment step was studied to increase the packing density of the PEM thereby achieving higher selectivities toward dissolved solutes. Here, it was shown that terminating a PSS/poly(allylamine) (PAH) multilayer with a single layer of Nafion, a highly fluorinated and therefore very hydrophobic polyelectrolyte, results in a 50% reduction in PEM swelling during membrane operation. This pronounced decrease in multilayer swelling was led to PEM membranes with desired properties such as higher selectivities towards micropollutants (pesticides, medicine, and hormones) and lower molecular weight cut-off (MWCO) values, albeit at the cost of small decreases in water permeability. The selectivity of these Nafion-containing PEM membranes was further improved when an asymmetric PEM structure was constructed. Here, coating of a Nafion/PAH multilayer on top of an already assembled PSS/PAH multilayer increased average micropollutant retentions to 97%. Interestingly, while the use of Nafion resulted in denser PEM membranes, salt retention remained similar, meaning that the retention of salts and organic solutes can be decoupled and separately tuned. This capability of PEM-based membranes is remarkable since for conventional polyamide based thin film composite nanofiltration membranes, the density of the layer strongly influences the retention of both salts and small organic solutes.

The ability to decouple salt and organic solute retentions is taken a step further in **Chapter 4**. Here, a different asymmetric PEM system is studied with the goal to create membranes that retain micropollutants but not salt. This concept is of great interest because it would allow removal of micropollutants from drinking water or from waste streams without altering the salt balance. Asymmetric PEMs with bottom layers of PSS/PAH and top layers of PAA/PAH were prepared. PSS/PAH is a more open PEM and is coated to ensure that the pores of the supporting hollow fiber membrane are fully closed. Conversely, PAA/PAH is a much denser PEM and this layer acts as the selective top layer or separation layer. Using this design, PEM membranes were fabricated with high water permeability ($12.8 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$), high micropollutant retentions (on average 98%), and low salt retention (10–15% of NaCl). Overall, this asymmetric design approach to creating PEMs results in membranes with unique separation properties, where the very thin ($\sim 4 \text{ nm}$) selective top layer determines the separation performance and gives the membrane a high water permeability.

In PEM membrane literature, most focus has been on just a few PEM systems (PSS/PDADMAC and PSS/PAH), and there is surprisingly little understanding on the role of specific polyelectrolytes in PEM membranes. For this reason, **Chapter 5** provides a fundamental characterization of PEMs combined with their membrane separation performances to obtain insight into the connection of PEM structure and separation properties. Specifically the role of the polycation is studied where PSS-based PEMs are prepared together with the vastly different PAH, poly(ethylene imine) (PEI), or poly(4-aminostyrene) (PAS). In addition, the effect of crosslinking by glutaraldehyde was studied since all polycations contain primary amines. By carefully studying the layer growth, excess charge, and separation properties, it was shown that PSS/PAS and PSS/PEI gave membranes that had an overall negative bulk and surface charge, whereas PSS/PAH gave positively charged membranes. These material properties resulting from the polycation chemistries could be directly coupled to PEM membrane performance. Here, PSS/PEI and PSS/PAS have high retentions toward Na_2SO_4 , whereas high retentions toward MgCl_2 were shown for PSS/PAH. In addition, it was shown that PSS/PAS membranes were very open with a permeability of $22 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$, whereas PSS/PEI membrane were denser and had permeabilities of just $4 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$. The density of the different PEMs was reflected in MP selectivity where PSS/PEI showed overall the highest retention. Moreover, a generic effect of crosslinking with glutaraldehyde was shown where for all PEMs, crosslinking resulted in denser and more selective PEM membranes at a cost of lower

permeability. The versatility of PEM membranes shown in this work with widely different separation properties allows for the choice of the optimal PEM for a specific application.

The two densest PEMs from the previous chapter, PSS/PAH and PSS/PEI, were subsequently studied for forward osmosis (FO). In **Chapter 6** the connection between PEM structure and FO performance is made and it is shown that PEM based membranes can be successfully used in FO when the right combination of PEM and draw solution is selected. The performance of both the PEM membranes was assessed using different draw solutions, namely NaCl, MgCl₂, MgSO₄, Na₂SO₄, and Na₃C₆H₅O₇ (trisodium citrate abbreviated to TSC), all at equal osmotic pressure. **Chapter 5** already showed that the PSS/PAH membrane is overall positively charged and the PSS/PEI is overall negatively charged. This charge behavior resulted in the PSS/PEI membrane having low reverse salt fluxes for the multivalent anions TSC and Na₂SO₄, whereas the PSS/PAH membrane showed the lowest reverse salt flux for a multivalent cation, MgCl₂, draw solution. This already shows that by combining the right PEM with the right draw solution, PEM membranes can operate effectively in a FO process. Interestingly, when retaining micropollutants during FO operation, Donnan–dialysis was observed where the sodium ions of the TSC draw solution selectively exchanged with the positively charge micropollutant atenolol. When the draw solution was changed to sucrose, containing no sodium ions, the atenolol retention increased sharply from –211% to positive retention values.

PEMs can also be combined with biomimetic membranes that are based on the natural water selective aquaporin protein. The aquaporin protein is stabilized into a robust polymeric vesicle called a proteopolymersome (150–200 nm) that is slightly positively charged. In **Chapter 7**, these two promising systems are combined to form proteopolymersome multilayers (PPMs) in combination with the polyanions; poly(acrylic acid) (PAA) and PSS. By carefully monitoring the PPM buildup, it was shown that PPMs can have good layer growth when the vesicles are alternately adsorbed for both PAA and PSS. The PPM where subsequently applied to the inside of hollow fiber support membranes to create PPM based membranes. Here, PAA based PPMs were shown to be defective in membrane performance experiments whereas PSS based membranes demonstrated very relevant NF performance. The PPMs did not show improved membrane performance in comparison to PEMs (PSS/PAH and PSS/PDADMAC), but the charge inside the multilayer was reversed to negative instead of the positive charge present in the PEMs. Combining PEMs and biomimetic approaches can lead to relevant NF membranes and add to the versatility of both systems.

As a whole, this thesis highlights that by only changing the ingredients of the deposition solution, by adding a post-treatment step, or by changing the design, widely different PEM membranes can be fabricated. The unique versatility of PEMs allows for precise control over layer properties which then translates into control over the PEM membranes separation behavior. Although no PEMs were created in this thesis that show an increased retention toward salt, in particular NaCl, denser PEMs with lower MWCO and higher micropollutant retention were constructed. Therefore, this thesis shows that salt and small organic molecule retention can be decoupled. For this reason, the future of PEM membranes will lie in the asymmetric design whether it is asymmetry induced by PEMs themselves, aquaporin containing layers, or other combinations.

Samenvatting

In dit proefschrift worden een aantal nieuwe methodes om de eigenschappen van polyelektroliet multilagen (PEM) voor membraantoepassingen te beïnvloeden, te manipuleren en te modificeren getoond. PEM zijn dunne polymeer filmen met een dikte variërende van 5 tot 50 nm. Ze zijn opgebouwd uit geladen polymeren, ook wel polyelektrolieten (PE) genoemd. Met behulp van de laag-bij-laag (LbL) methode kunnen polyanionen (negatief geladen PE) en polykationen (positief geladen PE) afwisselend geadsorbeerd worden op elk geladen oppervlak, onafhankelijk van de geometrische vorm. De LbL is een eenvoudige werkwijze waarbij elk gewenst substraat (bijv. een dragerstructuur) simpelweg ondergedompeld wordt in een waterige oplossing dat een kleine hoeveelheid PE (~ 0.1 g/L) en zout (0-0.5 M) bevat. Nadat de eerste PE laag op het substraat is gezet wordt het oppervlak afgespoeld waarna het ondergedompeld wordt in de tweede oplossing met de tegenovergesteld geladen PE. Op deze manier kan het aantal lagen met hoge nauwkeurigheid geconstrueerd worden, totdat de gewenste dikte van de PEM is bereikt. Bovendien kun je met de LbL methode de lading en dichtheid van de PEM beïnvloeden door simpelweg de zoutconcentratie, pH en polyelektroliet type in de oplossingen te wijzigen. In dit proefschrift wordt met 'PEM-dichtheid' de pakkingsdichtheid van polyelektrolieten in de multilaag en de bijbehorende zwelling bedoeld. De dichtheid kan worden beschouwd als de intrinsieke poriegrootte van de PEM – een dichtere PEM zal dus een kleinere poriegrootte hebben, wat resulteert in een hogere weerstand voor watertransport. PEM met een hogere zwellingsgraad zijn meer gehydrateerd en zullen derhalve een lagere dichtheid hebben, in tegenstelling tot PEM met een lagere zwellingsgraad. Door zijn eenvoudigheid en veelzijdigheid is de LbL methode zeer geschikt om nieuwe membraanmaterialen te maken. Dit aangezien PEM erg gemakkelijk gecoat kunnen worden op de binnenkant van holle vezel membranen, zogenoemde holle vezel nanofiltratie (NF) membranen. De mogelijkheid om de holle vezel geometrie te gebruiken is zeer aantrekkelijk, vanwege de kleinere aspectverhouding en verlaagde kans op vervuiling (geen afstandhouders nodig) in vergelijking met vlakke film membranen.

Het overkoepelend doel van dit proefschrift is het beïnvloeden van de scheidingseigenschappen van een PEM membraan en het dichter maken van de PEM voor een hogere scheidingselectiviteit van het membraan. Het hele proefschrift is gebaseerd op het variëren van de inhoud van de oplossingen waarin de PEM gesynthetiseerd worden.

Een veel gebruikt en goed onderzocht PE koppel voor het maken van PEM membranen is het polykation poly(diallyldimethylammonium chloride) (PDADMAC) in combinatie met het polyanion poly(natrium 4-styreensulfonaat) (PSS). Dit PE-koppel is zo grondig onderzocht omdat het resulteert in membranen met zeer goede scheidingseigenschappen en uitstekende chemische en fysische stabiliteit. De hoge stabiliteit betekent dat deze PEM-membranen gereinigd kunnen worden zonder de actieve scheidende laag te beschadigen en te degraderen. Echter, zoals in **Hoofdstuk 2** beschreven komt in deze PEM PDADMAC doorgaans in overmaat voor, wat zorgt voor een non-stoichiometrische verhouding. Dit heeft als gevolg dat de controle over de membraanlading en dus de scheidende eigenschappen verloren gaan. Dit resulteert in significante daling van sulfaatretenties van 94% tot wel 39%, wat duiding geeft voor een toenemend positief geladen oppervlak en bulk. In **Hoofdstuk 2** is op PEM-membranen voor de eerste keer aangetoond dat annealen met zout een belangrijke nabehandeling is om beheersing over de lading en dus scheidingseigenschappen te behouden. Annealen met zout voor de laatste PSS adsorptiestap heft het overmaatprobleem van PDADMAC op en leidt tot hogere sulfaatretenties, tot zelfs 97% bij een hogere permeabiliteit dan bij PEM membranen waar geen overmaat van PDADMAC aanwezig is.

In de vorige alinea is een nabehandelingstap benoemd om controle te hebben over de lading van het membraan, terwijl in **Hoofdstuk 3** een alternatieve nabehandelingstap is onderzocht om de pakkingdichtheid van PEM te verhogen en daarmee een hogere selectiviteit te behalen voor opgeloste stoffen. Hier is aangetoond dat met het eindigen van een PSS/ poly(allylamine) (PAH) multilaag met een enkele laag Nafion, een hoog gefluorideerd en dus zeer hydrofoob polyelektrolyet, leidt tot een halvering van de PEM-zwelling. Deze duidelijke daling in multilaag zwelling resulteert in PEM-membranen met gewenste eigenschappen zoals een hoge retentie voor microvervuilingen (pesticiden, medicijnen en hormonen). Daarnaast laten deze membranen een lagere molecuulgewichtsscheidingswaarde zien, zij het ten koste van een kleine daling in permeabiliteit. De selectiviteit van deze, Nafion houdende, PEM-membranen neemt verder toe als een asymmetrische PEM-structuur wordt gemaakt. Het coaten van een Nafion/PAH multilaag op een bestaande PSS/PAH multilaag verlaagt de poriegrootte en verhoogt microvervuiling retenties tot 97%. Opvallend is dat terwijl met het gebruik van Nafion de PEM-dichtheid verhoogt wordt, zoutretenties gelijk bleven, wat betekent dat retenties van zouten en organisch opgeloste stoffen ontkoppeld en apart afgestemd kunnen worden. Deze eigenschap die PEM gebaseerde membranen hebben is opmerkelijk aangezien met conventionele polyamide gebaseerde dunne film composiet NF-

membranen de retentie van zowel zout als ander opgeloste stoffen beiden sterk afhankelijk zijn van de dichtheid van de laag.

De eigenschap om de stofretenties van zout en organisch opgeloste moleculen te ontkoppelen wordt een stap verder gebracht in **Hoofdstuk 4**. Hier wordt een ander asymmetrisch PEM-systeem onderzocht met als doel om membranen te maken die wel microvervuilingen tegenhouden maar zout doorlaten. Dit concept is van groot belang om verwijdering van microvervuilingen van afvalstromen mogelijk te maken zonder de zoutbalans te veranderen. Asymmetrische PEM werden gemaakt met een onderlaag van PSS/PAH en een toplaag van PAA/PAH. De PSS/PAH laag is minder dicht en wordt gecoat om te zorgen dat de poriën van de draagstructuur volledig bedekt zijn. Daarentegen is de PAA/PAH laag veel dichter en gedraagt zich dus als de selectieve toplaag ofwel de scheidende laag. Met deze aanpak kunnen PEM-membranen gefabriceerd worden die hoge permeabiliteit ($12.8 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$), hoge microvervuiling retentie (gemiddeld 98%) en lage zout retenties (10–15% NaCl) hebben. In het geheel leidt deze asymmetrische benadering tot PEM-membranen met unieke scheidingseigenschappen waar een zeer dunne ($\sim 4 \text{ nm}$) selectieve toplaag het scheidende vermogen dicteert en toelaat dat het membraan zijn hoge water permeabiliteit behoudt.

In literatuur over PEM membranen wordt vooral gefocust op een paar PEM-systemen (voornamelijk PSS/PDADMAC en PSS/PAH) met verassend weinig inzicht over de rol van de specifieke PE in PEM-membranen. Om deze reden geeft **Hoofdstuk 5** een fundamentele karakterisering van PEM in combinatie met de scheidende eigenschappen van het respectievelijke PEM-membraan om inzicht te krijg in de relatie tussen PEM-structuur en de scheidingseigenschappen. In het bijzonder wordt de rol van polykationen onderzocht, hierbij wordt met PSS gebaseerde PEM in combinatie met de sterk verschillende PAH, poly(ethyleen imine) (PEI), en poly(4-aminostyreen) (PAS) gesynthetiseerd. Daarnaast wordt het effect van crosslinken met glutaraldehyde bestudeerd, aangezien alle gebruikte polykationen amines bevatten. Door het zorgvuldig bestuderen van de laaggroei, ladingsovermaat en scheidingseigenschappen wordt aangetoond dat PSS/PAS en PSS/PEI membranen een negatieve bulk- en oppervlaktelading hebben waartegen PSS/PAH positief geladen membranen zijn. Deze materiaaleigenschappen, resulterende uit de polykation chemie, kan direct gekoppeld worden aan de PEM membraan prestaties. PSS/PEI en PSS/PAS hebben hoge Na_2SO_4 retenties terwijl PSS/PAH hoge retenties voor MgCl_2 geeft. Bovendien wordt er aangetoond dat PSS/PAS membranen erg open zijn met een permeabiliteit van $22 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$, terwijl PSS/PEI membranen dicht zijn met een permeabiliteit van

$4 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$. De dichtheid van de verschillende PEM wordt weerspiegeld in de microvervuiling selectiviteit waar PSS/PEI de hoogste retenties geeft. Crosslinken van de verschillende multilagen met glutaraldehyde geeft een algemeen effect dat resulteert in dichtere en selectievere PEM-membranen, ten koste van de permeabiliteit. De veelzijdigheid van PEM-membranen met sterk uiteenlopende scheidingseigenschappen, getoond in dit hoofdstuk, maakt de keuze voor de ideale PEM voor een specifieke toepassing mogelijk.

De twee PEM met de meeste dichte structuur van het vorige hoofdstuk, PSS/PAH en PSS/PEI, worden vervolgens bestudeerd in toepassing van voorwaartse osmose (FO). In **Hoofdstuk 6** wordt het verband gelegd tussen PEM-structuur en FO-prestaties en er wordt aangetoond dat PEM-membranen succesvol toegepast kunnen worden wanneer de juiste combinatie van PEM en trekoplossing wordt gekozen. De prestatie van de PEM-membranen worden getoetst door het gebruik van verschillende trekoplossingen onder gelijke osmotische druk, namelijk NaCl, MgCl_2 , MgSO_4 , Na_2SO_4 , and $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ (trinatrium citraat afgekort naar TSC). **Hoofdstuk 5** toont aan dat PSS/PAH membranen positief geladen zijn terwijl PSS/PEI membranen negatief geladen zijn. Dit ladingskenmerk leidt bij PSS/PEI tot lage omgekeerde zoutfluxen voor multivalente anion houdende TSC en Na_2SO_4 trekoplossingen, terwijl het bij PSS/PAH leidt tot lage omgekeerde zoutfluxen met multivalente kation bevattende trekoplossingen, namelijk MgCl_2 . Dit toont aan dat bij gebruik van de juiste PEM-en-trekoplossing combinatie, PEM-membranen effectief kunnen functioneren in een FO-proces. Het is interessant dat wanneer microvervuilingen worden tegengehouden in FO, Donnan-dialyse geobserveerd wordt. De natriumionen van de TSC-trekoplossing worden selectief uitgewisseld met atenolol; een positief geladen microvervuiling. Wanneer de trekoplossing wordt veranderd naar een natrium loze sucrose oplossing, schieten atenololretenties omhoog van -211% naar positieve waarden.

PEM kunnen ook gecombineerd worden met biomimetische (geïnspireerd op biologische systemen) membranen gebaseerd op het natuurlijke, water selectieve aquaporine proteïne. Het aquaporine proteïne is gestabiliseerd in een robuuste polymeer vesikel of blaasje, ook wel proteopolymerosomen genoemd, 150-200 nm in grote en licht positief geladen. Deze twee veelbelovende systemen worden in **Hoofdstuk 7** gecombineerd om proteopolymerosomen multilagen (PPM) te maken met behulp van de polyanionen; poly(acrylzuur) (PAA) en PSS. Door het zorgvuldig bekijken van de PPM opbouw, wordt aangetoond dat PPM goede laaggroei hebben wanneer de vesikels afwisselend geadsorbeerd worden met dan wel PAA of PSS. De PPM zijn vervolgens op de binnenkant

van holle vezel membranen aangebracht om PPM gebaseerde holle vezel membranen te synthetiseren. Hierin wordt aangetoond, door middel van retentie experimenten, dat PAA gebaseerde PPM-membranen niet naar behoren werken terwijl degene gebaseerd op PSS goede NF-prestaties tonen. Er is geen sprake van een toegenomen membraanprestatie wanneer PPM worden gebruikt in plaats van PSS/PAH of PSS/PDADMAC PEM. Echter kan de lading in de multilaag worden omgekeerd van positief naar negatief als proteopolymerosomen gebruikt worden, in plaats van polykationen. Het combineren van PEM en biomimetische aanpakken kan leiden tot toepasbare NF-membranen en voegt veelzijdigheid toe aan beide systemen.

In zijn geheel onderstreept dit proefschrift dat uiteenlopende PEM-membranen gemaakt kunnen worden door simpelweg de ingrediënten van de adsorptieoplossingen te veranderen, nabehandelingstap uit te voeren of door het veranderen van het PEM-ontwerp. Deze unieke veelzijdigheid staat de nauwkeurige beheersing over de laageigenschappen toe, wat vertaald wordt in de controle over de scheidingseigenschappen van PEM-membranen. Hoewel er in dit proefschrift geen PEM gemaakt zijn die een verhoogde NaCl retentie geven, zijn dichter PEM met kleinere poriegrootte en hogere microvervuilingsretentie ontwikkeld. Derhalve toont dit proefschrift aan dat de retentiegraad van zout en kleine organische moleculen kan worden ontkoppeld. Om deze reden zal de toekomst van PEM-membranen in het asymmetrische ontwerp liggen door het gebruik van PEM of aquaporine bevattende lagen.

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About the author

Dennis Maik Reurink was born on the 27th of December 1990 in Emmen, the Netherlands. He grew up in the villages of Odoorn and Klijndijk and started high school in 2003 in VMBO on the Esdal college in Emmen. After two years he moved to HAVO and obtained his diploma in 2008 and subsequently his VWO diploma in 2010. In the same year he started his bachelor studies in Chemical Engineering and graduated in 2013 from University of Twente. After his bachelor studies, he continued his master studies in Chemical Engineering and specialized in Chemical and Process Engineering. During this time he performed an internship at Bayer Technology Services in Leverkusen, Germany for half a year modeling distillation columns. Furthermore, he co-organized a three week long study tour of C.T.S.G. Alembic to Chile. In 2016 he graduated his master studies at the Membrane Science and Technology group from University of Twente. In the same year, he started as a PhD candidate at the Membrane Science and Technology group under the supervision of Wiebe de Vos and Erik Roesink. The work presented in this booklet is the result of his PhD study.

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