Asymmetric polyelectrolyte multilayer nanofiltration membranes: Structural characterisation via transport phenomena

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A B S T R A C T

One promising application of polyelectrolyte multilayers (PEMs) is their use as selective layers in nanofiltration (NF). Especially encouraging are the simplicity of fabrication, controlled layer thickness in the nanometer range, and versatility. In addition to commonly used tuning parameters such as pH, ionic strength, and choice of polyelectrolytes, combining two different PEMs in a so-called asymmetric PEM enables further optimisation of the selective membrane layer. Experimental characterisation of these PEMs is complex, and therefore, the knowledge of the exact layer structure is limited. In this work, we combine filtration experiments and theoretical transport models to describe the effective structure of an asymmetric PEM made of a bottom layer of poly(allylamine hydrochloride) (PAH)/poly(sodium 4-styrenesulfonate) (PSS) and a top layer of PAH/poly(acrylic acid) (PAA). Obtained membrane properties suggest the formation of a distinct layer structure with individual layer properties close to the single symmetric PEM after a minimum number of layers. There is, however, a fundamental difference in the retention of salt and polyethylene glycol molecules. While salt retention properties of the asymmetric PEM are stable already after only one bilayer of PAH/PAA, a gradual transition in the retention of polyethylene glycol molecules from the more open PAH/PSS system to the dense PAH/PAA system is observed. This is attributed to the different exclusion mechanisms dominating solute transport (size- vs charge-based). A gradual decrease in molecular weight cut-off (MWCO) with increasing bilayer (BL) number of PAH/PAA is observed, resulting in a minimum MWCO of around 120 g mol\textsuperscript{−1} after 5 BLS. Theoretical transport models assuming an ideal layer structure in series predict this value as well. At the same time, high mono- to divalent salt selectivity is observed after 1 BL of PAH/PAA already. Single salt retention of NaCl is around 20% versus Na\textsubscript{2}SO\textsubscript{4}, MgCl\textsubscript{2} and MgSO\textsubscript{4} being above 95%. Although this trend is qualitatively predicted by the theoretical transport model, again assuming ideal layers in series, deviations indicate variations in charge distribution within these layers.

1. Introduction

The alternate deposition of oppositely charged polyelectrolytes, known as the layer-by-layer (LbL) method, to build polymeric films on a solid substrate was introduced more than 30 years ago by Decher et al. [1]. From that moment onwards, this promising concept of controlled fabrication of so-called polyelectrolyte multilayers (PEMs) has transformed into a highly studied and applied method to fabricate functional thin films. A number of excellent review articles [2–6] published over the years are evidence of the high interest in these materials. They also highlight the strengths and limitations of the LbL method, the progress made in the fundamental understanding of PEM structure, and the versatility of possible applications for PEMs (for example as stimuli-responsive materials [7,8] and membranes [9–14]). The key strengths of the LbL method are a fine control over PEM structures and functionalities (on the nanometer scale), with seemingly endless versatility, originating from the variety of components for and tuning parameters during deposition.

In search of sustainable and high-performance membranes to widen the range of applications and optimise existing membrane processes, LbL has been recognised as one promising “building block” to fabricate future membranes [15]. Especially in the field of nanofiltration (NF), membranes modified with PEMs have been proposed as an alternative to conventional commercial membranes [11,13,14]. In recent years, these membranes have been commercialised and are applied on industrial scale [16].

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The gold standard of commercial NF is thin-film composite (TFC) polyamide-based (PA) membranes fabricated via the interfacial polymerisation (IP) method [18]. Three key limitations of conventional polyamide-based thin-film composite (TFC) membranes are: low chlorine stability (limiting membrane lifetime) [18], membrane fouling (limiting process selectivity and efficiency) [19], and a membrane intrinsic selectivity-permeability trade-off (limiting process selectivity) [17,20,21]. PEM NF membranes with extraordinarily high resistance towards active chlorine [22] and harsh pH conditions (pH 0–14) [23] have been fabricated, allowing for chemical cleaning of membranes to remove fouling. Although fouling of NF membranes is inevitable [24,25], the extent can be mitigated by using PEMs. This includes the possibility of simple fabrication of hollow fibre (HF) NF membranes, which have been shown to have a lower susceptibility towards fouling compared to conventional spiral-wound membrane modules [26,27]. Alternatively, PEMs can be used to fabricate membranes with application-dependent anti-fouling properties by tuning properties such as surface charge and hydrophilicity [10,25,28,29]. Another powerful feature of PEMs as selective layers for NF membranes is the possibility to recycle severely fouled membranes by removal and reforming of the selective layer [30–32]. To address the selectivity limitations of conventional membranes, the Lbl method offers very controlled fine-tuning of PEM properties and the fabrication of tailor-made membranes. Although design criteria based on structure-performance relations to fully enable rational membrane design are still incomplete [12], several tuning parameters known from conventional Lbl have been applied for PEM NF membranes. Here we distinguish between the choice of constituents, the coating conditions, and post-treatment options. The most important components of PEMs are the polyelectrolytes. Here, one can vary the molecular weight [33], the pH sensitivity (often distinguished between weak and strong) [34,35] and functional groups [22]. In addition, the choice of support membrane [22,36–38] plays an important role. Once a choice has been made on polyelectrolytes, the coating conditions can be adjusted including the concentration of polyelectrolytes [39–41], the ionic strength of the coating solution [30,41–43], and the number of layers applied [36,44]. As an alternative to the traditional dip-coating method, a dynamic Lbl approach based on direct filtration of coating solutions to overcome diffusion-limited transport of polyelectrolytes can be used [45]. As a last step, the fabricated PEM can be further treated to increase layer stability via crosslinking [46,47] or fine-tune the charge balance via annealing [40,48].

One additional degree of freedom in Lbl, which we want to highlight separately, is the combination of more than one polyelectrolyte pair in one PEM structure. This concept was already applied in conventional Lbl to obtain thin films with advanced functionalities [49,50]. Also in the field of membranes, this has been identified as a promising parameter enabling a significant increase in performance [51–57]. Most notably, this coating strategy was recently applied by te Brinke et al. [56,57] to solve one limitation of coating very dense PEM films on a porous support, which is the trade-off in selectivity-permeability due to the necessity to obtain a defect-free separation layer. When a PEM layer is coated on a porous support, a minimum layer thickness is required to fill the underlying pores (the pore-dominated regime) until a defect-free selective PEM layer is obtained (the layer-dominated regime) [43]. The filled pores add to the overall hydraulic resistance of the PEM NF membrane but not to the selectivity [38]. Thus, an asymmetric PEM structure was proposed mimicking the concept of commercial TFC/asymmetric membrane structures: a support structure with less hydraulic resistance (here to fill the pores) and a separating layer with high selectivity (thickness down to 4 nm [56,58]). This structure is termed “asymmetric”, associated with the membrane structure, not to be confused with asymmetric growth related to the non-stoichiometric build-up of PEMs [42,59].

Little is known about the exact structure of these asymmetric PEM membranes and how it is related to the observed membrane performance. This is partly owed to the minimal film thickness and the relevance of water swelling (films have to be studied in the swollen state), strongly limiting the options for characterisation. Until now, properties such as film thickness, hydration, and layer interpenetration have been studied using neutron reflectometry [58] and ellipsometry [56]. By neutron reflectometry, a key property of the asymmetric PEM was indicated: despite a certain degree of interpenetration between the two types of PEMs, the structure is indeed truly asymmetric after a certain number of layers. It is important to note that this does not contradict the common interpretation of PEMs as “fuzzy” (highly intermixed) structures [60], as this typically happens over a limited number of layers with the diffusing species being extrinsic sites [61]. A distinct asymmetric structure is therefore possible. An
important question that results is: how does the structure of individual symmetric PEMs translate to the structure and transport properties of the asymmetric PEM NF membrane?

In this work, we explore the structure of asymmetric PEM NF membranes by studying transport phenomena through these films coupled with the use of theoretical transport models. The transport of uncharged solutes is nicely predicted by the simplified assumption of symmetric PEMs in series. This suggests that after a sufficient number of bilayers (BLs), an intrinsically dense structure of the top layer is obtained and unaffected by the bottom layer. The transport of charged solutes is more complex and non-intuitive due to the relevance of charge-based transport phenomena. Although the structure cannot unambiguously be determined in this case, theoretically assuming an idealised structure of the two symmetric PEMs in series does, again, qualitatively predict the experimentally observed transport behaviour. The result is a very high mono- to divalent-ion selectivity. This work paves the way for a more rational design of PEM NF membranes.

2. Experimental setup

2.1. Materials

Poly(allylamine hydrochloride) (PAH, \(M_n = 150\,000\) g mol\(^{-1}\), 40 wt.% in \(H_2O\)) was purchased from Nittobo Medical Co. (Japan). Poly(acrylic acid) (PAA, \(M_n = 250\,000\) g mol\(^{-1}\), 35 wt.% in \(H_2O\)), poly(sodium 4-styrenesulfonate) (PSS, \(M_n = 200\,000\) g mol\(^{-1}\), 30 wt.% in \(H_2O\)), polyethyleneimine (PEI, branched, \(M_n = 25\,000\) g mol\(^{-1}\)), magnesium chloride hexahydrate (\(\geq 99\%\)), sodium sulfate (\(\geq 99\%\)), magnesium sulfate heptahydrate (\(\geq 99\%\)), ethylene glycol (EG, anhydrous, 99.8%), diethylene glycol (DEG, 99%), polyethylene glycol 200 g mol\(^{-1}\) (PEG200, for synthesis), polyethylene glycol 400 g mol\(^{-1}\) (PEG400, for synthesis), glycerol (anhydrous, 99%–101%), sodium hydroxide (\(\geq 98\%\)), and hydrogen peroxide (29–31 wt.%) were purchased from Sigma-Aldrich. Sodium chloride (\(\geq 99.96\%\)) was kindly provided by AkzoNobel. Polyethylene glycol 600 g mol\(^{-1}\) (PEG6000, \(\geq 97.4\%\)), polyethylene glycol 2000 g mol\(^{-1}\) (PEG2000, \(\geq 97.8\%\)), and polyethylene glycol 3000 g mol\(^{-1}\) (PEG3000, \(\geq 98.8\%\)) were purchased from Merck. Polyethylene glycol 1000 g mol\(^{-1}\) (PEG1000, \(\geq 95.5\%\)) and sulfuric acid (95–97 wt.%), were purchased from ThermoFisher. Ethanol (96.2 vol.%) was purchased from Boom B.V. (the Netherlands). All chemicals were used without further purification. Two component polyurethane glue (2K Expert) was purchased from Bison. Hollow fibre (HF) ultrafiltration (UF) membranes made of modified polyethersulfone (PES) were kindly provided by NX Filtration B.V. (Enschede, the Netherlands). These membranes have a nominal molecular weight cut-off of 10 kDa, a pure water permeability of about 150 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\), and an inner diameter of 0.7 mm. For all \(H_2O\) solutions, MiliQ water with a resistance of at least 18.2 M\(\Omega\) cm was used.

2.2. Membrane fabrication

In this work, nanofiltration (NF) type membranes were fabricated by coating polyelectrolyte multilayers (PEMs) on top of a UF membrane with HF geometry. In the first step, the UF membrane was rinsed in a 10 vol.% ethanol in water solution for at least 24 h to flush out any preservatives. Subsequently, the UF membrane was rinsed with water. In the next step, a PEM was fabricated on top of the selective layer of the UF membrane using the layer-by-layer (LbL) method. The asymmetric pore structure of the UF membrane ensures that a cohesive selective layer is only formed on the inside of the HF. The LbL method comprises the exposure of a substrate to aqueous solutions of polycations and polyanions in an alternating fashion. The repeating step is commonly referred to as a bilayer (BL). One BL was fabricated by immersing the support into a polyion solution (0.1 g L\(^{-1}\) PAH, 50 mM NaCl, pH 6.0) for 15 min, rinsing (50 mM NaCl) the support three times for 5 min, immersing the support into a polyion solution (0.1 g L\(^{-1}\) PAA, 50 mM NaCl, pH 6.0; 0.1 g L\(^{-1}\) PSS, 50 mM NaCl) followed, again, by three times rinsing. Here we started the coating process with a polycation as the UF membrane charge is negative. The pH of dip coating solutions was adjusted using 0.1 M NaOH solution. In this work, three PEM membrane systems based on a previous study by te Brinke et al. [56] were investigated: [PAH/PSS]\(_{n}\), [PAH/PAA], and an asymmetric system built from [PAH/PSS]\(_{n}\) with [PAH/PAA] on top. Here \(n\) is the BL number. After coating the desired number of BLs, the membrane was rinsed in water and immersed in a 15 vol.% solution of glycero in water for at least 4 h. This step ensures the stability of the UF membrane pores during drying. Subsequently, the membrane was left to dry inside the fume hood under ambient conditions for at least 24 h. Modules for filtration measurements were made by gluing the as-prepared membranes into polyethylene tubing (6 mm outer diameter). A picture of a membrane module is shown in the Supporting Information S1.

2.3. Crossflow setup

All membrane filtration measurements were performed in crossflow operation at an outlet velocity of 1 ± 0.05 m s\(^{-1}\) for each fibre (corresponding to a Reynolds number of 700). Due to a permeate recovery of less than 1%, it is reasonable to assume that the inlet and outlet velocities are equal. Feed solution temperature was controlled at 20 ± 1°C. The transmembrane pressure was controlled in the range of 1–5 bar (depending on the type of membrane and measurement). The crossflow setup allows the operation of up to 16 modules in parallel. A schematic of the crossflow setup can be found in the Supporting Information S2.

2.4. Membrane performance evaluation

To evaluate the resistance of a membrane towards the permeation of water, the pure pater permeability was determined from filtration measurements with a pure water solution at three transmembrane pressure values: 1, 2, 3 bar ([PAH/PSS]\(_{1}\), [PAH/PSS]\(_{2}\), [PAH/PAA]1–4); 1, 3, 5 bar ([PAH/PAA], [PAH/PSS]1, [PAH/PAA]2, [PAH/PAA]3). The pure water permeability \(P_w\) (L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\)) was calculated based on the permeated mass of water \(m_w\) (kg) in a certain time frame \(t\) (h) relative to the applied pressure \(\Delta P\) (bar) by the following formula:

\[
P_w = \frac{m_w}{\rho_w \cdot A_m \cdot \Delta P} \tag{1}
\]

with \(\rho_w\) being the density of water (1 kg L\(^{-1}\)) and \(A_m\) the active membrane area (around 3.7 \(10^{-4}\) m\(^2\) for the used modules). The pure water permeability can be transformed into the hydraulic resistance \(R_h\) (m\(^{-1}\)) using the following formula:

\[
R_h = \frac{3.6 \cdot 10^{11} \cdot L \cdot P_w}{\eta \cdot \Delta P \cdot m} \tag{2}
\]

with \(\eta\) the dynamic viscosity of water (\(10^{-3}\) Pa s) and \(P_w\) with the units (L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\)).

To obtain qualitative information on the structural properties of the PEM membrane, the steric hindrance towards uncharged solutes was determined by measuring the retention of PEG of different molecular weights. Measurements were conducted at a \(\Delta P\) of 3 bar for [PAH/PSS]\(_{n}\) and [PAH/PSS]\(_{n}\), [PAH/PAA]1–8, and 5 bar for [PAH/PAA]1–8. Here the observed retention \(R_e\) (not corrected for concentration polarization) is defined as:

\[
R_e = 1 - \frac{C_p}{C_f} \tag{3}
\]

\(C_p\) and \(C_f\) are the mixing cup concentrations (mM) of the permeate and feed stream, respectively. The ratio of concentrations was determined via gel permeation chromatography (GPC), as described later. Two mixes of 1 kg m\(^{-3}\) for each PEG were used to prevent overlap of signal
performed to further ensure full cleaning of the wafer and activation. The wafer was thoroughly rinsed with water. Oxygen plasma treatment was conducted at a \( \Delta P \) of 3 bar for \([\text{PAH}/\text{PSS}]_{1-10} \) at 5 bar [62]. Three different mixtures (MgSO\(_4\) + Na\(_2\)SO\(_4\), MgCl\(_2\) + NaCl, and Na\(_2\)SO\(_4\) + Na\(_2\)CO\(_3\)) with a fixed sum of single salt concentration of 5 mM and varying ratio in the relative concentration of the salts (1:4, 2:3, 3:2, and 4:1) were used. For simplicity we have always used the same molar concentration. For more extensive studies it may be better to use constant ionic strength. The individual ion concentrations in the feed and permeate stream were determined via ion chromatography, as described later.

To allow the distinction between the Donnan exclusion mechanism (determined by membrane charge) and the dielectric exclusion mechanism (determined by dielectric properties of the membrane), ternary ion retention measurements were conducted for the symmetric PEM systems \([\text{PAH}/\text{PSS}]_{1-10} \) at a \( \Delta P \) of 3 bar and \([\text{PAH}/\text{PAA}]_{1-8} \) at 5 bar [63]. Three different mixtures (MgSO\(_4\) + Na\(_2\)SO\(_4\), MgCl\(_2\) + NaCl, and Na\(_2\)SO\(_4\) + Na\(_2\)CO\(_3\)) with a fixed sum of single salt concentration of 5 mM and varying ratio in the relative concentration of the salts (1:4, 2:3, 3:2, and 4:1) were used. For simplicity we have always used the same molar concentration. For more extensive studies it may be better to use constant ionic strength. The individual ion concentrations in the feed and permeate stream were determined via ion chromatography, as described later.

2.5. Analytical techniques

Single salt concentrations were determined by measuring the electrical conductivity of the aqueous solution using a portable conductivity meter (Cond 3310, WTW) and transforming that to a concentration based on calibration curves which can be found in the Supporting Information S3. PEG concentrations were determined via gel permeation chromatography (GPC). The GPC setup (Agilent 1200/1260 Infinity GPC/SEC series) consists of four columns (precolumn Suprema 8 × 50 mm 5 µm, 2x Suprema 1000 Å × 300 mm, Suprema 30 Å × 5 µm × 300 mm). Polymer Standards Service GmbH) in series and a refractive index detector (Agilent 1100 HPLC G1362 A RID Detector). The flow rate of the eluent (50 mg L\(^{-1}\) Na\(_2\)SO\(_4\) in H\(_2\)O) was 1 mL min\(^{-1}\). The detector signal as a function of time for one PEG mix consists of 4 peaks that partially overlap. To distinguish the components, fitting via Gaussian functions was done for peak deconvolution. The peak height is directly proportional to solute concentration and can therefore be applied directly in the calculation of solute retention using Eq. (3).

Individual ion concentrations in ternary ion mixtures were determined via ion chromatography (IC). The IC setup (858 Professional Sample Processor, 2x Eco IC, Metrohm) consists of an anion column (Metrosep A Supp 17 - 150/4.0), a suppressor for the anion analytes in series and a refractive index detector (Agilent 1100 HPLC G1362 A RID Detector). The flow rate of the eluent (50 mg L\(^{-1}\) Na\(_2\)SO\(_4\) in H\(_2\)O) was 1 mL min\(^{-1}\). The detector signal as a function of time for one PEG mix consists of 4 peaks that partially overlap. To distinguish the components, fitting via Gaussian functions was done for peak deconvolution. The peak height is directly proportional to solute concentration and can therefore be applied directly in the calculation of solute retention using Eq. (3).

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2.6. Ellipsometry

Layer thickness and swelling of the different PEM systems on a model surface (SiO\(_2\)-on-Si wafer with 80 nm thick thermal oxide layer) was measured via Ellipsometry. The fabrication of PEMs on top of the silicon wafer is analogous to the membrane fabrication using the LbL method as described in 2.2, where the initial layer of PAH was replaced by PEI (0.1 g L\(^{-1}\) PEI, 50 mM NaCl, pH 6.0) as a precursor layer to obtain homogeneous surface coating and smooth films [63,64]. Before coating, the top surface of the silicon wafer was cleaned using a small amount of piranha solution (3 mL H\(_2\)SO\(_4\) + 1.5 mL H\(_2\)O\(_2\)). After 1 h the wafer was thoroughly rinsed with water. Oxygen plasma treatment was performed to further ensure full cleaning of the wafer and activation of the surface. Ellipsometry measurements were performed in nitrogen atmosphere (400 mL min\(^{-1}\) N\(_2\) flow, J.A. Woollam M-2000 XI, EC-400) and in the presence of water (J.A. Woollam M-2000 V, EC-400). To translate the measured change in polarisation of light (amplitude ratio \(\tan(\Phi)\) and phase difference \(\Delta\)) with a range in wavelength of 380–1000 nm, data analysis was performed using the J.A. Woollam CompleteEASE software package. The optical model that was built consists of the following layers: Si-SiO\(_2\)-PEM. The dependency of refractive index on the wavelength of light for the PEM layer was described via a Cauchy relationship:

\[
n(\lambda) = A + \frac{B}{\lambda^2} \tag{4}
\]

with \(n\) being the refractive index (–) dependent on wavelength \(\lambda\) (nm), and \(A\) (–) and \(B\) (nm\(^2\)) the two Cauchy constants. Both Cauchy parameters and the dry layer thickness of the PEM were fitted to the measurements in N\(_2\) atmosphere after the signal was stabilised (around 90 min). The optical model for measurements in an aqueous environment was extended by an effective medium approximation (Bruggeman, BEMA) to account for the incorporation of water in the film.

\[
0 = \Phi_d \frac{n_{\text{dry}}^2 - n_{\text{wet}}^2}{n_{\text{dry}}^2 + 2n_{\text{wet}}^2} + \Phi_{\text{H}_2\text{O}} \frac{n_{\text{H}_2\text{O}}^2 - n_{\text{wet}}^2}{n_{\text{H}_2\text{O}}^2 + 2n_{\text{wet}}^2} \tag{5}
\]

Where \(\Phi\) is the volume fraction (–) and \(n\) the refractive index (–). The indices indicate the two individual media, here the dry PEM (\(\text{dry}\)) and water (H\(_2\)O) that make up the effective medium (\(\text{wet}\)), which is the wet PEM film. Due to rapid swelling, the signal would stabilise much quicker for these measurements (15 min). The following ratio defines swelling (SR):

\[
S_R = \frac{d_{\text{wet}} - d_{\text{dry}}}{d_{\text{dry}}} \cdot 100\% \tag{6}
\]

Here \(d\) is the layer thickness (nm) of the PEM in water (\(\text{wet}\)) and in N\(_2\) atmosphere (\(\text{dry}\)).

3. Theoretical transport model

In the following the theoretical transport model that was applied will be shortly introduced. The full system of equations can be found in the Supporting Information S4.

3.1. PEG retention

A pore flow model was applied to translate retention measurements of PEG molecules to an intrinsic membrane characteristic. Here, the selective layer is represented by cylindrical pores with an effective pore size. The two fitting parameters that characterise the different PEM layers are the effective membrane thickness \(\Delta x\) and the effective pore radius \(r_p\). These parameters are used for the qualitative comparison of different membranes. They do not claim to display the actual physical structure of the polyelectrolyte network (which is likely of a much more irregular nature).

In a previous study, we have shown that a single pore size cannot fully represent the retention of PEG molecules with a wide range of molecular weights [65]. Such a pore size distribution was introduced. The distribution is represented by a log-normal function, which extends the set of parameters by replacing the effective pore radius \(r_p\) with an effective mean pore radius \(r_m\) and its spread \(\sigma\).

In both cases, fitting parameters were determined based on pure water permeability measurements in combination with PEG retention measurements.
ter permeability and MgSO\textsubscript{4} PAH/PAA) followed by membrane characterisation based on pure wa-

tures and obtain a defect free film. For this purpose, an increasing BL support, a certain layer number is required to close the underlying

4.1. Polyelectrolyte multilayer growth

4. Results and discussion

3.2. Salt retention

Membrane transport of ionic solutions was described via the Donnan steric pore model and dielectric exclusion (DSPM&DE) model [66, 67]. This model combines the extended Nernst–Planck equation (ion transport via advection, diffusion, and electromigration) with an equilib-

rium partitioning term at the solution-membrane interface (Donnan-, dielectric-, and steric exclusion). A bundle of cylindrical pores with a single pore size represents the selective layer. In addition to the parameters describing these ideal pores, an effective volumetric charge density \( \epsilon \) and an effective relative dielectric constant inside the pores \( \epsilon_r \) describe the charge-based exclusion mechanisms.

As discussed later, the steric exclusion (including steric hindrance coefficients for diffusion and convection) was not included for ion transport. Here, fitting parameters are determined based on pure water permeability and PEG retention measurements for \( \Delta x_r \), and ternary ion retention measurements (as shown in [62]) for \( \epsilon \) and \( \epsilon_r \). The system of equations was solved using the algorithm developed by Geraldes et al. [68].

3.3. Asymmetric membrane

As an attempt to gain a more fundamental understanding of the structure and transport processes in novel asymmetric PEM membranes, the layer was represented by two single layers with properties of the individual symmetric PEMs in sequential configuration (as schemati-

cally shown in Fig. 1). From a previous study on the intrinsic structure of (identical) asymmetric PEMs using neutron reflectometry [58], it was confirmed that the individual layers are indeed (except for some interlayer mixing of around 2 BLs) distinct. The mathematical im-

plementation of the two layers in series consists of imposing local thermodynamic equilibrium at the interface of the two layers.

4. Results and discussion

We organise our results into four sections: (1) the layer growth of the studied PEM systems and the influence on hydraulic membrane resistance, (2) the transport of uncharged solutes, (3) the transport of charged solutes, and (4) the implications on selective layer structure.

4.1. Polyelectrolyte multilayer growth

To fabricate functional PEM based NF membranes on top of an UF support, a certain layer number is required to close the underlying pores and obtain a defect free film. For this purpose, an increasing BL number was coated for both symmetric PEM systems (PAH/PSS and PAH/PAA) followed by membrane characterisation based on pure wa-
ter permeability and MgSO\textsubscript{4} retention (can be found in the Supporting Information S6). Based on these measurements the minimum number of BLs required to reach the layer-dominated regime were determined as 7 for PAH/PAA and 8 for PAH/PSS.

To ensure that the observed membrane performance can be related to PEM layer properties, complete membrane characterisation was performed for the following systems: [PAH/PSS]\textsubscript{7−11}, [PAH/PAA]\textsubscript{7−10} and [PAH/PSS]\textsubscript{8} + [PAH/PAA]\textsubscript{4}. For NF membranes, one property determining the hydraulic resistance of water concerns the thickness of the selective layer (R\textsubscript{\text{h}}). Assuming that only the thickness of the selective layer varies in the layer-dominated regime (intrinsic PEM properties constant), the hydraulic resistance represents the layer growth. The intrinsic PEM properties (such as network mesh size and water content) of different PEM systems can vary, affecting the slope and absolute value of hydraulic resistance as a function of BL number.

Fig. 2 displays pure water permeability and hydraulic resistance for the studied PEM systems. The main motivation for an asymmetric PEM becomes apparent when comparing the pure water permeability of the symmetric systems. PEM NF membranes based on PAH/PSS have a significantly higher permeability than PAH/PAA membranes when reaching the layer-dominated regime. This indicates that filling the underlying support pores with the less permeable PAH/PAA largely diminishes the membrane performance. The asymmetric PEM system, where the pores are filled with PAH/PSS, displays a significantly higher pure water permeability than the PAH/PAA system, continuously drop-

ping with PAH/PAA BL number on top. To relate filtration performance to layer properties, one can compare the hydraulic resistance of the systems. In addition to the overall higher resistance of the PAH/PAA system, the slope of resistance with BL number is much higher com-
pared to PAH/PSS (20 fold). This could be caused by a higher thickness increment and/or a smaller effective pore size for PAH/PAA (discussed in the following section). For the idealised assumption of both systems being unaffected by each other, growing fully linearly (constant thickness increment) and having constant intrinsic properties, the slope in hydraulic resistance of the asymmetric system and the PAH/PAA sys-

tem should be equal. It is clear that for the initial 3 BLs this assumption is oversimplified. Instead of linear growth, a non-linear increase in hydraulic resistance is observed. Only after 3 BLs is the growth linear. The final slope of the asymmetric system does, however, approach the same order of magnitude as the pure PAH/PAA system (about 40% smaller).

The delayed layer growth in the first few BLs of PAH/PAA on top of PAH/PSS was further confirmed with thickness measurements on a model surface using ellipsometry. Values for the thickness of the dry asymmetric system in the nitrogen atmosphere are shown in the Sup-

porting Information S6. Here, the thickness of the asymmetric system is well below that estimated from linear growth based on the symmetric PAH/PAA system. Despite the apparent non-linear growth, quantitative differences are evident in the hydraulic resistance and ellipsometry measurements. We attribute this to the different substrates and the difficulty in directly relating film thickness to effective membrane
thickness. Since the swelling of all systems was around 40% with no statistically significant difference, wet thickness measurements are not shown. Although a similar degree of swelling is expected for the studied systems, there may be slight differences that are not resolved by our ellipsometry measurement. For studying slight variations in swelling (also with local resolution over the film thickness), neutron reflectometry, as performed in [58], is recommended. We ascribe the delayed growth behaviour to the known supralinear (often termed “exponential”) growth of PAH/PAA, also observed in [56,58]. Supralinear PEM growth is typically ascribed to the mobility of polyelectrolytes (respectively their intrinsic/extrinsic sites [61]) and the resulting penetration depth of the coated layer. This penetration depth is large for PAH/PAA (coated at pH 6) due to the high mobility of the polyelectrolytes, leading to exponential growth until a certain layer thickness [33,69]. PAH/PSS is known to form strong and glassy complexes, leading to linear PEM growth [33,70,71]. Consequently, the PAH/PAA system coated on top of PAH/PSS, despite some interpenetration between the layers [58], effectively resembles the coating on an impenetrable substrate.

4.2. Uncharged solute retention

To evaluate the transport of uncharged solutes through the different PEM systems, the retention of PEG molecules of relevant molecular weight for NF membranes was determined. Due to the absence of electrostatic interactions, the transport is assumed solely determined by steric restrictions (here represented by an effective membrane pore size).

Fig. 3 displays the observed retention as a function of PEG molecular weight and the fitted pore size distribution for both symmetric systems just after reaching the layer-dominated regime. Fitting parameters can be found in the Supporting Information S7. Since the PEG retention does not vary significantly with BL number, only one BL number is shown for each system. The PAH/PAA system displays a smaller and sharper pore size distribution compared with the PAH/PSS system, with higher retention towards the PEG molecules. Based on the charge density of the polyelectrolytes, one expects a higher ionic cross-linking density of the PAH/PAA system (one bond per 6 carbon atoms) than the PAH/PSS system (one bond per 11 carbon atoms) [72]. This results in a molecular weight cut-off (MWCO) of around 110 g mol⁻¹ for the PAH/PAA membrane and around 350 g mol⁻¹ for the PAH/PSS membrane. For applications where high removal of organic molecules is required, the MWCO should be as low as possible. This, however, typically comes at the cost of high hydraulic resistance. The idea of the asymmetric system is to combine the low hydraulic resistance of the PAH/PSS system with the low MWCO of the PAH/PAA system.

Fig. 4 displays the observed PEG retention for the asymmetric system as a function of PAH/PAA BL number on top of 8 BLs of PAH/PSS,
4.3. Charged solute retention

Another property of PEM NF membranes that is crucial for the application and can give information about the layer properties is the retention of charged solutes (especially ions). One commonly used method in membrane characterisation is the evaluation of single salt retention. Here we test the retention towards salts made of both monovalent and divalent cations and anions.

In Fig. 5 single salt retention for the systems \([\text{PAH/PSS}]_{8-11}\) and \([\text{PAH/PAA}]_{7-10}\) is shown. One common feature of NF membranes is the relatively low NaCl (monovalent salt) retention. Despite slight variations with increasing BL numbers, the NaCl retention remains fairly constant at around 28% for PAH/PSS membranes and 32% for PAH/PAA membranes. The retention of salts containing divalent ions is much higher, caused by a combination of Donnan exclusion (high retention for divalent co-ions) and dielectric exclusion (high retention for all divalent ions). The confidence intervals for the MgCl\(_2\) retention by the PAH/PSS system are very large, caused by variations in the membrane modules (4 for each system). This is confirmed by a repeat of single salt retention and similar trends in ternary ion retention of Mg\(^{2+}\) ions (see Supporting Information S8). Still, one can extract a reasonable MgCl\(_2\) retention for this system by assuming that the retention does not change too much with BL number and taking the average from all measurements. Here a MgCl\(_2\) retention of 59% is estimated. Retention towards NaSO\(_4\) and MgSO\(_4\) by this system is again relatively constant, with an average around 97% and 90%, respectively. Overall this indicates that the PAH/PSS system (ending with PSS) has a negative excess charge, causing relatively higher retention for NaSO\(_4\) than MgCl\(_2\). Based on previous studies on the PAH/PSS system, one expects an excess of PAH and an effectively positive membrane [73]. One potential explanation for the effectively negative membrane is the relatively low ionic strength during coating (0.05 M NaCl) combined with the negative top layer of PSS. The PAH/PAA membrane also displays high mono-/divalent salt selectivity. However, the retention seems to be dominated by the dielectric exclusion mechanism. The average retention for all divalent ions is similar: 78% for NaSO\(_4\), 79% MgCl\(_2\) and 86% MgSO\(_4\). The significant drop in retention at 4 BLS after pore closing (10 BLS) coincides with a jump in MWCO from around 140 Da for 3 BLS to around 290 Da for 4 BLS after closing (see Supporting Information S9). We attribute this to defects in the multilayer and their increased influence at lower membrane permeability.

For the asymmetric PEM membrane \([\text{PAH/PSS}]_{1} + [\text{PAH/PAA}]_{4-6}\), a surprisingly high mono-/divalent salt selectivity is observed right from the first BL of PAH/PAA (see Fig. 6a). This behaviour is rather unexpected based on previous results. To better compare the different systems directly, average values of single salt retention for the first 4 BLS after pore closing for each system are shown in Fig. 4b. In contrast to uncharged solute retention, where a gradual transition behaviour of up to 4 BLS of PAH/PAA was observed (see Fig. 4), the salt retention is already fully established after one BL of PAH/PAA on a pore closed membrane by PAH/PSS. This suggests that steric exclusion plays a minor role in single salt retention, in contrast to what the theoretical model predicts (based on ion Stokes radius and effective pore radius). We conclude that the pore size determined by PEG retention does not correctly describe the steric exclusion of ions. Thus, the steric exclusion term (including hindrance factors) is neglected when modelling salt retention. Also, the very high retention for all divalent salts (>93%) and, at the same time, relatively low retention for NaCl (around 19%) is, at first glance, counter-intuitive based on the behaviour of the individual symmetric systems. This will be further discussed in the following with the help of theoretical transport models. Lastly, despite large variations in membrane performance for the symmetric PAH/PSS system (especially in the presence of Mg\(^{2+}\)), the asymmetric membranes display highly reproducible and very constant performance with increasing BL number (except for a continuous decrease in Na\(_2\)SO\(_4\) retention from 95% to 90%). The very high salt selectivity of the asymmetric PEM NF membrane already achieved after coating 1 BL of PAH/PAA on top of the PAH/PSS system (resulting in a pure water permeability of 9.1 m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\)) makes this membrane very promising for applications such as softening [46] and salt purification [74].
In an attempt to gain a more fundamental understanding of this counter-intuitive transport behaviour of salts, a transport model (DSPM&DE) was applied with a very simplistic membrane representation of two layers in series (neglecting any transient zone due to interpenetration of the two systems and any interaction between the two layers). Although this view is simplified and the physical meaning of fitting parameters in this model is limited, we hope to obtain at least a better qualitative understanding of the transport. Also, the exact selective layer structure cannot be determined unambiguously, theoretically or experimentally. Based on neutron reflectometry studies [58] on the thickness and swelling distribution of these asymmetric membranes, we expect the proposed asymmetric layer structure to represent the actual film structure qualitatively.

In the first step, the charge-based fitting parameters of the model have to be determined. Since there are two parameters describing Donnan exclusion (effective charge density) and dielectric exclusion (effective dielectric constant), the parameter set cannot be determined unambiguously from single salt retention measurements. Here we use the method proposed by Déon et al. [62], where these parameters are determined from ternary ion retention measurements at different ion compositions. The two parameters can be fitted for each composition with three ions present and then extrapolated to single salts. One such set of ternary ion retention using a combination of NaCl and MgCl\textsubscript{2} in varying molar ratios is displayed in Fig. 7. Ternary ion retention results for other salts using these membranes can be found in the Supporting Information S10. What all these measurements have in common, is the accelerated transport of the more mobile counter-ion to a common co-ion. This even leads to negative ion retention and is caused by the spontaneously formed electrical potential gradient due to the more abundant and highly retained counter-ion (e.g. negative Na\textsuperscript{+} retention in the presence of dominant MgCl\textsubscript{2}). This effect is more severe for a lower concentration of the mobile counter-ion, i.e. low Na\textsuperscript{+}/Mg\textsuperscript{2+} ratio. The retention of ions that compose the dominant salt converges towards the respective single salt retention. Lastly, these measurements display large confidence intervals observed in the presence of Mg\textsuperscript{2+}. Based on individual module retention (not shown here) and much smaller confidence intervals for other systems, the uncertainty is attributed to variance in membrane modules and not the measurement method.

Using the extrapolated fitting parameters, the single salt retention of the symmetric systems is predicted (see Fig. 8). For the PAH/PSS system, the parameters could not be unambiguously determined for the ternary mixture of MgSO\textsubscript{4} + Na\textsubscript{2}SO\textsubscript{4} to extrapolate properties in the presence of MgSO\textsubscript{4}. Thus, the effective charge density was determined from fitting single salt retention assuming an effective dielectric constant of 35 (similar to the PAH/PAA system). Overall, the theoretically predicted retention matches reasonably well. The large overestimation of MgCl\textsubscript{2} retention for the PAH/PSS system is attributed to the high variance in measured retention. Here, the prediction for the membrane module with minimum and maximum Mg\textsuperscript{2+} ion retention in ternary ion measurements is indicated in the figure. For the PAH/PAA system, the retention of the divalent salts is consistently overestimated. In an alternative procedure, only the effective dielectric
constant was extrapolated from ternary ion retention measurements, followed by fitting the effective charge density to single salt retention measurements. Supporting Information S11 illustrates the parameter extrapolation method based on ternary ion retention. Furthermore, the parameters determined for both approaches are given. Both approaches will be compared for the prediction of the asymmetric membrane performance in the following.

Both ellipsometry (see Supporting Information S6) and hydraulic resistance (see Fig. 2) measurements strongly suggest supralinear growth of the PAH/PAA system on top of the PAH/PSS membrane. As shown in more detail in the Supporting Information S12, the naive assumption of linear growth in effective membrane thickness significantly overestimates the hydraulic resistance. Therefore, the effective membrane thickness parameter was calculated from pure water permeability results of the asymmetric PEM membrane.

The single salt retention for an ideal asymmetric system of the two symmetric layers in series is compared to the experimentally observed one in Fig. 9. In the case of fitting parameters based on ternary ion retention, uncertainty in retention for the symmetric PAH/PSS system in the presence of MgCl₂ translates to the asymmetric system. For MgCl₂, the minimum and maximum predicted retention are displayed. Since the PAH/PAA layer dominates the retention in the model, the variation is much smaller than for the single salt case of PAH/PSS. Considering the simplified assumption of the asymmetric layer structure (and the DSPM&DE model), the predicted retention of the asymmetric system matches reasonably well.

In the case of effective charge density fitted to single salt retention measurements, prediction for NaCl and Na₂SO₄ is similar to the previous method, again matching quite well. For MgCl₂ the uncertainty due to large module variations for PAH/PSS this time affects the retention of the asymmetric membrane more severely. Here, on average, the MgCl₂ retention is considerably underestimated. Also, the MgSO₄ retention is significantly underestimated, however, less than for MgCl₂. Compared to the fitting parameters fully based on ternary ion retention, the predicted retention of the asymmetric system for MgCl₂ and MgSO₄ is less accurate.

To understand the theoretically predicted retention of the asymmetric PEM membrane, one can compare it to the predictions for the two symmetric systems, [PAH/PSS]₈ and [PAH/PAA]₇. A trend of the retention being determined by the symmetric layer with the higher retention is observable. This matches qualitatively to the principle of a bipolar membrane, where high retention for divalent ions can be obtained [75,76]. Since, in this case, both symmetric systems already have high retention for divalent anions and cations, the effect is less severe.

4.4. Selective layer structure

The theoretical model has clear limitations to unambiguously determining the structure of the asymmetric PEM layer (especially considering charge-based properties). Already the structure of a symmetric PEM is likely more accurately described by accounting for a distribution in charge rather than a homogeneous charge density [77]. However,
Fig. 9. Comparison of experimentally observed (blue) and predicted single salt retention (red) of asymmetric PEM systems. By extrapolation of both charge-based fitting parameters (left) and by extrapolation of only the dielectric constant while fitting charge density to single salt retention (right). The shaded red bar indicates the maximum and minimum prediction based on single modules. Error bars display 95% confidence intervals.

Fig. 10. Schematic illustration of asymmetric PEM structure, based on PAH/PSS and PAH/PAA.

without additional confirmation on the internal structure, this just increases the number of fitting parameters. Here, further studies with a larger number of different asymmetric PEM membranes are required, in addition to more advanced complementary characterisation techniques. However, we want to suggest a structure of the asymmetric PEM layer that can explain results from characterisation techniques (ellipsometry \[56\] and neutron reflectometry \[58\]), PEG retention and ion retention, and is based on previous studies on the structure of symmetric PEM systems \[3,5,6\]. Fig. 10 shows a sketch of the proposed film structure.

Starting with the bottom layer of PAH/PSS and ending on the negative polyelectrolyte PSS, we expect an excess of PSS at the film-liquid interface with a more loose structure and chains dangling into the solution. The charged groups are mostly associated with mobile counter-ions in this region (extrinsic compensation). This excess charge of the PEM surface is expected to cause additional protonation of PAH in the bulk of the PEM (since PAH is a weak base) \[78,79\]. This leads to a slight excess positive charge and the well-known odd-even effect of swelling for this system. According to observed single salt retention measurements, an effectively negatively charged selective layer is formed, indicating that the charge of the surface layer still dominates ion transport. Upon adding PAH/PAA BLs, we want to distinguish two phases based on the observed transition in PEG retention.

During the transition phase, layer growth is affected by the interpenetration with the PAH/PSS film below \[49,58\] and the initial phase of exponential layer growth \[33,34,69\]. The interpenetration between both systems is expected to be relatively low, due to the glassy nature of PAH/PSS \[70,71\]. From neutron reflectometry \[58\], a BL number of 2 is given. However, one has to keep in mind that the initial layers are relatively thin, so the actual thickness of interpenetration might not be too large. Based on the observed transition for PEG retention, the intermixing zone is expected to feature a gradual change in structural properties based on both symmetric systems. Consequently, the PEG retention only slowly increases with BL number. Once a highly intrinsically compensated dense bulk layer of pure PAH/PAA has been formed, the PEG retention of the symmetric PAH/PAA system is reached.

Salt retention, on the other hand, does not show this transition region, and we attribute this to charge-based exclusion being the dominant mechanism for salts. The Donnan potential is mainly determined by the PEM surface and hence not dependent on the formation of an intrinsically compensated bulk layer. Based on this, indeed, no delayed transition would be expected. Donnan potential induced by the PAH/PAA film alone can, however, not explain the high retention of all divalent salts. We can think of two potential causes for the observed salt retention behaviour: a charge distribution resembling a bipolar membrane or dominant dielectric exclusion. Since dielectric exclusion seems to be the dominant mechanism in both symmetric systems and retention of the asymmetric PEM is reasonably well predicted, the latter seems more likely. Further studies resolving the extrinsic charge distribution in these films using radio-labelling techniques could give valuable insight. Quantitative differences between the theoretically predicted and the observed salt retention indicate that the intrinsic properties related to the charge-based exclusion of the individual symmetric systems are affected by the presence of the other system. Two potential effects are variations in excess charge and a reduction of defects (and their relative influence) due to reduced roughness of the substrate when coating PAH/PAA on top of PAH/PSS.
A coherent intrinsically compensated dense bulk zone of PAH/PAA is developed in the final phase of asymmetric PEM growth, starting from 5 BLS of PAH/PAA. Compared to the symmetric PAH/PSS film, PAH/PAA forms an effectively denser layer, likely caused by the higher charge density of polyelectrolytes involved [72]. Again, in this first theoretical study of asymmetric PEMs, we chose to keep the model film structure as simple as possible and neglect any transition layer to approach the problem with limited bias and a limited number of fitting parameters.

We do not claim the generality of the proposed structure but expect it to be highly dependent on the chosen symmetric PEM system. Parameters that can strongly influence the build-up of the asymmetric film include the degree of interpenetration between the layers and the type of layer growth, both determined by polyelectrolyte mobility. Again, this asks for more extensive research on different types of asymmetric PEMs.

5. Conclusion and outlook

In this work, the structure of asymmetric PEM-based NF membranes was investigated via a combination of filtration experiments and theoretical transport models. The membrane is built from a symmetric PEM of PAH/PSS to fill the underlying pores of the UF support at a reduced cost of membrane permeability. On top of the PAH/PSS layer, a denser PAH/PAA PEM is built to achieve higher retention towards small organic molecules (MWCO down to 120 g mol⁻¹). The asymmetric PEM membrane shows distinct behaviour for uncharged and charged solute transport. A very high mono- to divalent ion selectivity is achieved already after 1 BL of PAH/PAA on top of the PAH/PSS layers. On the other hand, the retention of PEG is gradually improving with increasing BL number of PAH/PAA and only reaches a stable retention equal to that of the symmetric PAH/PAA system after 5 BLS. This difference is explained by the different mechanisms dominating the transport of PEGs and ions. While steric exclusion determines the retention of PEGs, charge-based membrane properties dominate the retention of ions. Intermixing between the two symmetric PEMs causes a slow transition from the more open PAH/PSS to the more dense PAH/PAA system, determining PEG retention. Transport models successfully predict the retention of PEG molecules when the dense bulk structure of PAH/PAA is developed. Salt retention is dominated by charge-based exclusion mechanisms, which depend on excess charge and the effective dielectric constant of the PEM. These are immediately developed after 1 BL of PAH/PAA. Here we propose two potential mechanisms for the observed retention: dominant dielectric exclusion or a bipolar charge distribution. The transport model qualitatively predicts salt retention but does not allow for an unambiguous determination of the exact charge distribution in these asymmetric PEMs. Consequently, the exact retention mechanism is still unclear. As observed in previous studies on this system, results suggest a truly distinct layer structure of the asymmetric PEM. Deviations from theoretically predicted ideal transport are attributed to intermixing between the two symmetric PEMs and intrinsic charge-based properties being influenced by each other. An exciting feature of these membranes is the option to tune MWCO independently from salt retention.

CRediT authorship contribution statement


Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Dr. J de Grooth currently holds a position at NX Filtration B.V., a membrane manufacturer. The other authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request

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Appendix A. Supplementary data

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