Kosmotropes and chaotropes: Specific ion effects to tailor layer-by-layer membrane characteristics and performances

Citation for published version (APA):
Kosmotropes and chaotropes: Specific ion effects to tailor layer-by-layer membrane characteristics and performances

Anna Casimiro, Cees Weijers, Daniëlle Scheepers, Zandrie Borneman, Kitty Nijmeijer

ABSTRACT

So-called specific ion effects strongly impact physicochemical phenomena in among others, morphologies of polymeric membranes. This can be correlated to the identity of the ions, rather than just to their charge or concentration. We use this effect to tune the properties of layer-by-layer membranes prepared with the polyelectrolytes polydiallyldimethylammonium chloride and polystyrene sodium sulfonate. To systematically study these, membranes were prepared using different salts (NaBr, NH₄Cl, MgCl₂, NaCl, LiCl, MgSO₄, NaH₂PO₄, (NH₄)₂SO₄, Na₂SO₄). The specific ion effects were evaluated thanks to the classification of salts and PEs into kosmotropes (well hydrated) and chaotropes (poorly hydrated) following the law of matching water affinities (LMWA). The impact of the type of anions and cations on the multilayer formation and membrane performances was evaluated. Membranes prepared with kosmotropic salts achieved stable performances after only 4 bilayers, and almost 6 times higher water permeabilities than membranes prepared with chaotropic salts without compromising and often even improving the membrane’s size exclusion behaviour. The salts used tuned the membranes charge: Kosmotropic salts delivered negatively charged membranes with NaCl, MgCl₂ rejections till 97% and 10% respectively, while chaotropic salts formed more positively charged membranes with reversed behaviour with Na₂SO₄ and MgCl₂ rejection of 20 and 89%.

1. Introduction

With a view to establish sustainable development, water scarcity must be addressed and processes that are aimed to water purification and recovery of valuable solutes are being developed continuously [1, 2]. Among these processes, membranes have a prominent role due to their ease of application, adaptability to the process and efficiency [3, 4]. The success of this technology is ascribed to the concerted rational design of efficient processes and the development of new membrane materials that can perform according to the rejection/recovery requirements. A specific category of membranes, nanofiltration (NF) membranes, gained significant attention thanks to their high fluxes and recovery of valuable solutes are being developed continuously [1, 2]. Among these processes, membranes have a prominent role due to their ease of application, adaptability to the process and efficiency [3, 4]. The success of this technology is ascribed to the concerted rational design of efficient processes and the development of new membrane materials that can perform according to the rejection/recovery requirements. A specific category of membranes, nanofiltration (NF) membranes, gained significant attention thanks to their high fluxes and recovery of valuable solutes are being developed continuously [1, 2]. Among these processes, membranes have a prominent role due to their ease of application, adaptability to the process and efficiency [3, 4].

The Layer-by-Layer (LbL) technique is an efficient, cheap and easily tunable method for NF membrane preparation [5]. It consists of the deposition of several oppositely charged polyelectrolyte (PE) layers on top of a porous support. The nanometer thickness of the LbL layer often guarantees high water permeabilities while the presence of charges and ionic linkages between the PEs imparts charge and size selectivity to the membranes. Great scientific effort has been devoted to the investigation of several LbL assembly parameters and their influence on the resulting membrane performance [6]. Parameters that were explored in detail are the selection of the PE couple, the effect of their concentration, the influence of layer coating time and rinsing time, the impact of temperature of the coating solutions and their ionic strength.

The latter in particular, delivers impactful modification of the membrane multilayer structure without costly PE modification or concentration increase and can even shorten the lengthy LbL membrane assembly time. For example, if the PEs are coated in the absence of any additional salt (ionic strength of the salt solution equal to zero), the formation of the multilayer assembly involves the direct interaction of the charges of the polyanion (PA) with the ones of the polycation (PC) giving rise to so-called intrinsic charge-compensation [7–10]. With increasing ionic strength, the charges of the PEs can be shielded and compensated by the salts dissolved in the solution. This leads to extrinsic charge-compensation and the formation of thicker, less dense layers that can improve the water permeabilities of the membranes obtained [11]. Despite the extent of scientific effort dedicated to the investigation of...
several LbL preparation parameters [6], tuning the effect of extrinsic charge compensation has been often limited to the use of NaCl in various concentrations. The use of salts different from NaCl has not been researched systematically, although it is a very effective and simple tool to tune actual membrane filtration performance. As a matter of fact, it is known that the nature of the salt (and the ions from which it is made of) dissolved in an aqueous solution has extensive consequences for the solubility of the macromolecules present and their interactions [12,13]. This concept was initially studied to explain the change in protein solubility in water in the presence of different salts by Franz Hofmeister with the Hofmeister series of ions [13] and has been developed ever since. In the following paragraphs, a brief description of the Hofmeister series and the so-called “specific ion effects” will be given together with a more detailed explanation of the concepts used in this work.

While shedding light on the mechanistic reasons behind the specific ion effects is far from the scope of this work, these effects are omnipresent in literature and have very important consequences on several polymer properties [14–16]. In particular in the case of PE, it has been demonstrated that different salts have a great impact on the assembly of multilayers [17–22]. The simple tuning of the salt nature can lead to thinner or thicker layers, more open or denser structures, hydrophilic or hydrophobic assemblies.

The versatility of the salt tuning approach and the ease of its application offers an extremely valuable tool for the membrane world. Controlling the nature of the salts used during the LbL membrane coating process can thus be used to steer membrane performances. Even though there is a significant body of literature available on the fundamental understanding and impact of specific ion effects on polymer multilayer formation [10,17,18,20,22–25], their applicability and impact on LbL membrane formation and performance is still unexplored.

For this reason, in this work we examine the use of different types of salts on the preparation of LbL membranes and their effect on membrane performances. The results are contextualized in the spectrum of specific ion effects, not only regarding the influence of the salts but, most importantly, their contribution effects and to the more accepted terminology of “specific ion effects”. Even though there is no definite agreement on the mechanisms responsible for these effects, giving rise at times to controversial approaches [27], several reports have agreed on the validity of the work of Collins on the “law of matching water affinities” (LMWA) [28]. According to this approach, ions are classified based on their degree of hydration into kosmotropes (well hydrated) and chaotropes (poorly hydrated). The rule states that the formation of ion pairs between ions of opposite charge is favored if their hydration enthalpies $\Delta H_h$ (water affinity) match (Table 1). That is, kosmotropic anions easily form ion pairs with kosmotropic cations while their tendency to bind chaotropic cations is lower. Moreover, the viscosity coefficient $B$ is used as a measure of the interaction of the ions with water and of their charge density. Ions are then classified into kosmotropes if their Jones-Dole viscosity coefficient $B$ is positive and as chaotropes if it is negative (Table 1). Henceforth, in this work only the classification of ions into kosmotropic/chaotropic will be used.

Most importantly, these effects are not limited to the interaction between the anion/cation of an inorganic salt. In an aqueous solution containing the inorganic salt and a charged polymer (a protein or as in this work a PE), these specific ion effects are not exclusively driven by the salt nature but also by that of the polymer specificity [15]. This is bound to the nature of the functional groups of the polymer repeating unit, their charge density and their hydrophilicity [32,33]. For example, considering the low charge density of their monomer unit [32,33] and the negative value of the viscosity coefficient $B$ of their respective charged groups [27], PDADMAC and PSS can be classified as chaotropic.

Following this, the tendency of the PEs and selected ions to form ion pairs is schematically visualized in Fig. 2.

### Table 1

<table>
<thead>
<tr>
<th>Ion</th>
<th>$\Delta H_h$ (kJ/mol)</th>
<th>$B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$^{2+}$</td>
<td>1921^a</td>
<td>0.385^a</td>
</tr>
<tr>
<td>Li$^+$</td>
<td>519^a</td>
<td>0.150^a</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>409^a</td>
<td>0.086^a</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>307^a</td>
<td>$-0.007^a$</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>1059^b</td>
<td>0.208^b</td>
</tr>
<tr>
<td>H$_2$PO$_4^-$</td>
<td>522^b</td>
<td></td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>381^a</td>
<td>$-0.007^a$</td>
</tr>
<tr>
<td>Br$^-$</td>
<td>347^a</td>
<td>$-0.032^a$</td>
</tr>
</tbody>
</table>

*a29*, ^b30*, ^c31*
3. Experimental

3.1. Materials and chemicals

PDADMAC (Mw = 200–350 kg/mol, 20 wt% in water), ammonium sulfate (\((\text{NH}_4\text{H}_2\text{SO}_4, \text{Mw} = 132.14 \text{ g/mol})\) and polyethylene glycols (PEGs) with different molecular weights (Mw = 200, 400, 600, 1000, 2000, 4000 g/mol) were supplied by Sigma-Aldrich (The Netherlands). PSS (Mw = 500–700 kg/mol, 20.4 wt% in water) was provided by Tosoh Organic Chemical Co. LTD (Japan). Sodium chloride (NaCl, Mw = 58.44 g/mol) was supplied by AlfaAesar. Sodium sulfate decahydrate (Na\(_2\text{SO}_4\cdot10\text{H}_2\text{O}, \text{Mw} = 222.20 \text{ g/mol})\) was obtained from Fluorochem BV (UK). All chemicals were used as supplied.

Hollow fiber tight ultrafiltration membranes (HFS 60 membranes) were used as membrane support on which the PE layers were coated. The HFS 60 membranes were kindly provided by Pentair X-Flow (The Netherlands). The hollow fiber membrane support consists of polyethersulfone (PES) which is modified to carry negative charges. The hollow fiber bundles were immersed in water/EtOH (18 wt% EtOH in water) overnight and then rinsed with deionized water before coating. PE coating solutions containing 0.01 wt% of PDADMAC (or PSS) and 0.5 M ionic strength of one of the salts (NaBr, \(\text{NH}_4\text{H}_2\text{SO}_4\), NaCl, LiCl, MgSO\(_4\), NaH\(_2\text{PO}_4\), (NH\(_4\))\(_2\text{SO}_4\) and Na\(_2\text{SO}_4\)) were prepared. Rinsing solutions of 0.5 M ionic strength of one of the salts studied were prepared. The choice of using the same molar ionic strength for all the salts derives from the necessity to account for the non-ideality of the solutions [35]. The molar concentration of the salts was then for NaBr, NaCl, LiCl and NaH\(_2\text{PO}_4\) of 0.5 M, for MgCl\(_2\), (NH\(_4\))\(_2\text{SO}_4\) and Na\(_2\text{SO}_4\) of 0.167 M and for MgSO\(_4\) of 0.125 M. The salts used were chosen to evaluate both the effect of chaotropic/kosmotropic character of cations and anions and their charge (monovalent/divalent).

The hollow fiber bundles were immersed first in the PDADMAC coating solution (30 min with 5 min of manual refreshment) and after in the rinsing solution of the respective salt used (30 min with 10 min manual refreshment) forming one PE layer. After this process, the bundles were immersed in the PSS coating solution (30 min with 5 min of manual refreshment) and finally the rinsing step was repeated. Two oppositely charged layers (PDADMAC/PSS) form one bilayer. The procedure was repeated until 7 bilayers (14 individual PE layers) were coated on the support. After each layer rinsing step, 8 fibers were taken and stored in the respective salt solution for characterization. Nine bundles of LbL membranes were prepared in this way each with a different salt.

3.3. Characterization methods

3.3.1. Reflectometry

The growth of the PE multilayer was quantitatively measured using optical fixed-angle reflectometry, which allows for an in-situ and quantitative measurement of the adsorbed amount of PEs on top of a silicon wafer. A monochromatic He/Ne laser (Newport, 1108 P) (power<1 mW) was projected onto a BK7 glass prism (refractive index at a wavelength of 632.8 nm = 1.5151) inside a flow cell. The silicon wafer was placed in the cell and had a silicon oxide layer on top with a thickness of 49.5 nm (as determined by ellipsometry). The polarized laser was directed towards the wafer and the beam was reflected on its surface at the Brewster angle (70°). This resulted in a parallel and a perpendicular component of the beam (I\(_{p}\) and I\(_{s}\)) respectively of which the intensity was measured. The original ratio of both components (defined as S\(_{0}\)=I\(_{p}\)/I\(_{s}\)) changes upon adsorption of PE on the silicon wafer surface.

The PE multilayer was formed by first feeding a PDADMAC solution (0.01 wt% of PE and 0.5 M ionic strength of the salt selected) to the flow cell for 5 min. Subsequently, the wafer was rinsed with a salt solution of the same ionic strength for 5 min. After rinsing, a PSS solution (0.01 wt% of PE and 0.5 M ionic strength of the salt selected) was passed through the cell for 5 min. After the PSS coating, the wafer was rinsed in the same manner as after the PDADMAC coating step. This cycle produced one bilayer (two monolayers) and this was repeated until 7 bilayers (14 monolayers) were coated on the silicon wafer.

The difference between the signal obtained after PE adsorption and S\(_{0}\)=5-S\(_{p}\) is proportional to the amount of PE adsorbed (\(\Gamma, \text{mg/m}^2\)):

\[
\Gamma = \frac{Q_{t}}{S_{p}} \Delta S
\]

in which \(Q_{t}\) (mg/m\(^2\)) is the quality factor. This is dependent on the refractive index increment (dn/dc, ml/g) of the PEs. The dn/dc was determined using an Optilab rEX refractometer at a wavelength of 589 nm. The differential refractive index at concentrations of 10 g/L, 5 g/L, 2.5 g/L and 1.25 g/L in 0.05 M NaCl was determined with respect to a reservoir solution containing 0.05 M NaCl. The dn/dc for PDADMAC was found to be 0.1802 ml/g and for PSS 0.199 ml/g.

Knowing the dn/dc values, the thickness of the silicon oxide layer and \(\Delta S/S_{0}\) Q\(_{t}\) values were calculated using Prof. Huysgens software from Dullware iterating the process for each monolayer adsorbed. The adsorption amounts I\(_{p}\) are thus, calculated for every PE monolayer.

3.3.2. Zeta potential

Streaming potential measurements were performed to evaluate the
apparent zeta potential, hence the surface charge of the LbL membranes prepared. An electrokinetic analyser (SurPASS™ Anton Paar, Austria) was used. The streaming current was generated by flowing a 5 mM KCl solution along the hollow fiber membrane. One sample was measured for 10 cycles at room temperature and constant pH (~5.8). The values obtained were corrected for the cell constant (length and cross section of the membrane samples) and the apparent zeta potential was calculated with the following equation:

$$
\zeta = \frac{dI}{dP} \cdot \eta \cdot \varepsilon_0 \cdot \Delta \varepsilon
$$

in which $$\zeta$$ is the apparent zeta potential (V), I is the streaming current (A), P is the pressure (Pa), $$\eta$$ is the dynamic viscosity of the electrolyte solution (Pa s), $$\varepsilon$$ is the dielectric constant of the electrolyte solution (−), $$\varepsilon_0$$ is the vacuum permittivity (F/s), L is the length of the membrane sample (m) and A is the cross section of the membrane channel (m²).

### 3.3.3. Water permeability and salt retention performance

To evaluate the performance of the LbL membranes prepared, water permeability and the salt retention were measured. For reproducibility evaluation, 6 membrane fibers per layer were measured using a cross-flow membrane cell following the procedure described by Refs. [11,36]. A nominal flow of 6 L/min at atmospheric pressure and a trans-membrane pressure of 3 bar were applied resulting in 7.8 m/s with a minimum Reynolds number of 6000 through the fibers.

For the evaluation of the water permeability, demi water was used as feed and the permeate volume was collected for at least 10 min. The collected fractions were weighted and the water permeability L (L/ m²bar) was calculated with equation (3):

$$
L = \frac{V_p}{A \cdot t \cdot \Delta P}
$$

in which $$V_p$$ is the permeate volume (L), t is the permeation time (h), A is the fiber filtration area (m²) and $$\Delta P$$ is the effective pressure (bar).

To determine the salt retention performances of the membranes prepared, 5 mM salt solutions of MgSO₄, NaSO₄, MgCl₂ and NaCl were respectively used as feed and the permeate was collected after at least 10 min. The salt retentions were then calculated following a previously reported method [11].

### 3.3.4. MWCO

A PEG solution was prepared using 1 g/L of each PEGs at different Mw (200 g/mol, 400 g/mol, 600 g/mol, 1000 g/mol, 2000 g/mol and 4000 g/mol). The solution was then used as feed in the same set-up used for the evaluation of water permeability and salt retentions. Feed and permeate samples were then filtered through a 0.22 μm filter and analyzed via gel permeation chromatography (GPC) (Shimadzu LC-2050C 3D series) with one size exclusion column (Shodex OHpak SB-802.5 HQ 8 × 300 mm² column 200 Å, 6 μm). The flow rate of the GPC solution samples was 1 ml/min, and the eluent used was ultrapure water (PURELAB Option). The concentration of the feed and permeates were determined via GPC analysis with refractive index measurements (RID-20 A) as a function of the molecular weights of the PEGs. The MWCO was defined as the corresponding PEG molecular weight at which 90% retention is observed.

### 4. Results and discussion

#### 4.1. Reflectometry

To evaluate the effect of the different salts used on the mass adsorption of the PE layers, reflectometry experiments were carried out (Fig. 3).

As can be seen in Fig. 3, the nature of the salts has a severe influence on the adsorption behaviour of the PE. The order of PE adsorption follows the series:

$$
NaBr > NH₄Cl > MgCl₂ > NaCl > LiCl > MgSO₄ > NaH₂PO₄ > (NH₄)₂SO₄ > NaSO₄
$$

To explain these trends, it is valuable to first assess the PEs growth mechanism based on the anions in the salts, secondly to scrutinize the influence of the cations and finally, to evaluate the specific effects on the mass adsorption per specific PE layer (PDADMAC or PSS).

Firstly, the effect of the anions is addressed as it is known that due to their higher ability to interfere with the H-bonded structure of water [37], anions have a stronger influence on PEs than cations [28,38]. In Fig. 2 it can be noticed that all the salts containing chaotropic anions (Br⁻, Cl⁻) result in significantly higher mass adsorption compared to the salts containing kosmotropic anions (H₂PO₄⁻, SO₄²⁻). Knowing that the PEs studied are chaotropes following the LMWA, the added chaotropic ions (Br⁻, Cl⁻) have the tendency to form strong ion pairs with the PEs.

In the case of PDADMAC, this translates into the formation of favourable interactions especially with Br⁻. The salt that shows the highest mass adsorption is indeed NaBr (dark green in Fig. 2). This is expected since the Br⁻ ion possesses a very pronounced chaotropic character (Table 1) and moreover, it is considered to act as a plasticiser for PDADMAC [39]. This plasticising action has no effect on the actual amount of ions interacting with the PC, but does bring Br⁻ close to PDADMAC and by doing so shields its charges, extrinsically compensates them, weakens its interaction with PSS and leads to higher free volume [39–42]. Unsurprisingly, consequently to the deposition of a large amount of PDADMAC, also more PSS needs to adsorb to compensate for the previously deposited charges (Fig. 4a).

After an initial linear growth for the salts containing chaotropic anions (Br⁻, Cl⁻), the higher mass adsorption leads to exponential growth of the multilayers (SI, Fig. S1). The higher extrinsic charge compensation of PDADMAC due to chaotropic anions has been associated also to higher looping of the PE in the layer, hence less dense, more thick and rough multilayers [17,20,22].

On the other side of the LMWA instead, the lowest mass adsorption is observed for the SO₄²⁻ containing salts which, unlike Br⁻, has a marked kosmotropic character due to its high ΔHₚ and positive viscosity coefficients (Table 1). Once more, this is expected due to the unfavourable ion pairing with the chaotropic PDADMAC: kosmotropic ions.
preferentially interact with water molecules rather than with PEs, resulting in less extrinsic charge compensation, hence less shielding by the countermolecules making the PE readily available to electrostatically interact with the charges of the opposite PE (Fig. 4b) [18]. This translates into almost perfectly linear growth of the multilayer (Figure SI). An exception is MgSO$_4$ for which, despite the presence of a strong kosmotropic anion, exponential growth is shown (Fig. 2). This peculiar behaviour is caused by the divalent nature of Mg$^{2+}$ which results in the formation of stronger interaction with PSS compared to monovalent cations [43], allowing for strong extrinsic charge compensation and a seemingly chaotropic character for MgSO$_4$ [44]. For this reason, this salt will be considered as borderline in the rest of this work.

The observation of the growth regime of the PE based on the nature of the anions used in this work brings a clear classification; Salts that contain anions with a marked chaotropic character (Br$^-$, Cl$^-$) give rise to exponential growth, the ones that contain kosmotropic anions (H$_2$PO$_4^-$, SO$_4^{2-}$) show linear growth. In the following paragraphs for simplicity the salts will be classified accordingly following exclusively the nature of their anions: chaotropes or kosmotropes.

Next, even though the anions have a stronger influence on the PE interactions, also the effect of the cations must be addressed. That is because the performance properties of the final membranes are the product of the interplay of effects arising from the individual contribution of anions and cations (and PEs). In the specific case of chaotropic salts containing Cl$^-$ and a monovalent cation (NH$_4$Cl, NaCl, LiCl), the order of mass adsorption they give rise to is directly explained through the LMWA. Giving the chaotropic nature of PSS, stronger chaotropic cations have a higher tendency to extrinsically compensate the PE charges (Fig. 4). Similarly, also the order of mass adsorption of kosmotropic salts is related to the nature of the cations. Except for the already mentioned case of MgSO$_4$, SO$_4^{2-}$ containing salts show a mass adsorption trend that follows the LMWA ((NH$_4$)$_2$SO$_4$ > Na$_2$SO$_4$). A special case is MgCl$_2$ for which, despite the high kosmotropic character of Mg$^{2+}$ (Table 1), an overall chaotropic behaviour of the salt is observed. This is due to the already seen effect of Mg$^{2+}$ which effectively shields the charges of PSS but mostly, to the presence of the chaotropic Cl$^-$, albeit an indirect effect: The strong chaotropic character of Cl$^-$ results in strong interactions with PDADMAC giving rise to relatively high PE mass adsorption. This high amount of positive PE charge must be compensated, hence an unexpectedly high amount of PSS adsorbs on the surface, compensating the charges of PDADMAC.

Finally, aside from comparing the total mass adsorptions obtained with the different salts, it is interesting to take a closer look at the values obtained for the mass adsorption per layer, i.e. bilayer 6.5 and 7. In the case of NaBr due to its excessively high adsorption at higher bilayers, resulting in limitations in the experimental measurement method, the mass adsorption for bilayer 4.5 and 5 is reported (Fig. 5).

Besides showing once more that NaBr results in significantly higher mass adsorption compared to the other salts due to its strong chaotropic character, there is a distinct difference between the odd (solid bars in
Fig. 5) and even (striped bars in Fig. 5) bilayers. For salts containing a chaotropic anion that has a stronger chaotropic character than the associated cation (NaBr, NH$_4$Cl, NaCl, LiCl) (Fig. 2), the mass adsorption is higher for the odd bilayers (PDADMAC terminated, solid bars in Fig. 5) than for the even ones (PSS terminated, striped bars in Fig. 5). Again this is due to the strong interaction of the anions with PDADMAC [18]. This trend is switched for the other salts in the series (MgSO$_4$, Na$_2$SO$_4$, NaH$_2$PO$_4$, (NH$_4$)$_2$SO$_4$) giving the stronger chaotropic character of their cations compared to the anions. An exception is again MgCl$_2$ for which, despite the strong chaotropic character of Cl$^-$, higher mass adsorption of PSS is observed. This is related to the strength of the interaction between PSS and Mg$^{2+}$ and its divergent nature which makes Mg$^{2+}$ effective in extrinsically compensating the charges of PSS [43]. This shielding effect is higher compared to the one generated by Cl$^-$ on PDADMAC leading to more mass adsorption of PSS.

Overall, this confirms that the nature of both anions and cations, their interactions with each other and with the PEs cooperatively define the final characteristics of the multilayer and the performances of the membranes prepared in this work. Furthermore, they corroborate the theory that salt effects in PEs systems must be addressed as a combination of cation, anion and polymer specific effects.

### 4.2. Apparent zeta potential

To develop an understanding of the charged nature of the membranes prepared with different salts, apparent zeta potential measurements were performed (Fig. 6). On the left-hand side of Fig. 6 the values obtained for the terminating layers coated with chaotropic salts are shown, whereas on the right side the values for the kosmotropic salts are reported.

A clear trend can be observed: the membranes prepared with chaotropic salts show overall a considerably less negative zeta potential compared to the ones prepared with kosmotropic ones, which are clearly negative, confirming that the use of different salts not only has an influence on the PE adsorption behaviour, but it also has an important effect on the surface charge of the membranes prepared. This is a consequence of the interactions of the PEs with the salts used in the coating solution and is closely connected to the results obtained with reflectometry.

As previously shown (Fig. 5), the adsorption of PDADMAC compared to PSS is higher when using chaotropic salts due to charge shielding effect of the anions (Br$^-$, Cl$^-$). This guarantees the presence of a higher amount of positively charged groups on the membrane surface when coating them with chaotropic salts thus, a less negative (i.e. more positive) surface charge for the multilayer assembly. Vice-versa, when using kosmotropic salts in the LbL coating solution, the charges of PSS are more shielded than the ones of PDADMAC giving higher deposition of the polyanion. This ensures the presence of more negative functionalities throughout the thickness of the membranes and a surface charge sharply more negative.

A more detailed look at the odd-even effect is valuable to evaluate the specific influence of anions/cations of the salts employed on the surface charge of the membranes prepared. Significant differences between odd and even layers are found for the membranes. Except for the membranes prepared with NaBr, MgCl$_2$, and MgSO$_4$, all the membranes show a more negative zeta potential for the PSS terminated layers than for the PDADMAC ones. This is intuitive giving the negatively charged nature of the sulfonic acid groups of PSS and the positive nature of PDADMAC (Fig. 1). Nevertheless, the membranes coated with NaBr, MgCl$_2$, and MgSO$_4$ show the opposite: Bilayer 6.5 has a more negative zeta potential than bilayer 7.

For the NaBr coated membranes, the interaction of PDADMAC with Br$^-$ causes the more negative zeta potential of the PSS, Br$^-$ has a strong ability to interact with PDADMAC due to the strong chaotropic nature and to penetrate the electric double layer resulting in effective shielding of the PDADMAC charges [45]. Furthermore, as previously mentioned, the use of chaotropic ions gives a higher looping of the PE chains and to higher swelling of the polymer in water. This effect is particularly evident in the presence of Br$^-$ [46] and it is known to lower the zeta potential [47].

For the membranes prepared with MgCl$_2$ and MgSO$_4$, the higher values found for the zeta potential of PSS than for PDADMAC terminated layers are a consequence of the interactions between Mg$^{2+}$ and PSS. The formation of interactions between negatively charged surfaces and divalent cations (i.e. PSS and Mg$^{2+}$) is known to be the result of an electrostatic contribution and of quantum mechanical dispersion forces [48]. The latter are responsible for excessive charge compensation and in this case even charge neutralization of the PE, even resulting in so-called charge reversal or overcompensation [48,49] and thus higher values for the zeta potential of PSS compared to PDADMAC terminated layers.

### 4.3. Membrane performance evaluation

#### 4.3.1. Water permeability

To evaluate the effect of the different salts used in the coating process on the performances of the membranes, water permeability measurements were carried out (Fig. 7).

When discussing the results in Fig. 7, two aspects need to be addressed: the effect of the salt on the terminating PE layer and that on
the multilayer as a whole.

Firstly, the individual PEs give rise to an odd-even effect that shows an interesting trend. All the membranes prepared with chaotropic salts (NaBr, MgCl₂, NH₄Cl, NaCl, LiCl) show higher water permeabilities for the PDADMAC terminated layers (solid bars in Fig. 7) than for the PSS terminated ones (striped bars in Fig. 7). In line with the discussion above, the presence of chaotropic anions during coating results in more open coiled structures. Also, chaotropic ions induce higher swelling of PDADMAC, hence the formation of more open structures and higher water permeabilities [22]. In addition, due to its higher mobility in the multilayer, PDADMAC can swell up to 4 times more than PSS which gives rise to higher water permeabilities as well [50–52]. Moreover, it is known that the ionic effect associated with the presence of chaotropic anions in the vicinity of PDADMAC causes its swelling, hence the formation of more open structures and higher water permeabilities [22].

For the membranes prepared with kosmotropic salts this trend is switched: PSS terminated layers have higher water permeability than PDADMAC terminated ones. In this case, the anions (SO₄²⁻, H₂PO₄⁻) preferentially interact with water instead of with PDADMAC which in turn, tightly pairs with PSS. The charges of the latter are subsequently more extrinsically compensated due to the higher chaotropic nature of Na⁺, which causes again coiling of the PSS chain more open layers. This translates into higher water permeabilities for the PSS terminated layers.

Secondly, Fig. 7 shows a clear trend for the water permeability results: The membranes containing kosmotropic anions have higher water permeabilities. This is especially true for the membranes prepared with Na₂SO₄ that, for bilayer 7, have a water permeability almost 6 times higher than those prepared with NaBr (~18 vs ~3 L/m²hbar).

This may read counterintuitive considering the above for which chaotropic ions give rise to more swelling and higher water permeabilities. That is in fact only applicable though to the systems studied before they reach an exponential growing regime (Fig. S1). Fig. S2 shows that initially, during the linear growth phase, the water permeability of the membranes prepared with NaBr is indeed higher than that of the membranes prepared with Na₂SO₄. When the growing regime of membranes prepared with NaBr switches to exponential growth (approximately at bilayer 2.5, Fig. S1) the higher amount of mass deposited induces higher resistance to water transport hence, lower water permeabilities.

Giving the findings obtained with reflectometry showing the deposition of thicker layers for the chaotropic salts, these results are not surprising. The membranes prepared with kosmotropic salts consists of thinner layers consequently leading to higher water permeabilities. Membranes prepared with MgSO₄ though form an exception. As seen before, this salt contains a kosmotropic cation (Mg²⁺) that leads to strong charge shielding of the PSS charges [48]. This result in the formation of a thicker layer because of the strong interaction of the cation with PSS, and thus, lower water permeability.

In addition to the explanations above, there is another factor that has an influence on the water permeability: the hydrophilicity of the multilayer assembly [53–55]. As previously discussed, the interaction between the chaotropic ions and the PEs results in charge shielding and the formation of contact ion pairs [28,56]. Moreover, chaotropic ions are known to have a rather weakly bound hydration shell and are considered hydrophobic [12]. The availability of the PE charges is instead, superior when the membranes are prepared using kosmotropic salts. This makes them more prone to interact with the oppositely charged PE but also with water molecules via H-bonding. In addition to this, kosmotropic salts are by definition more hydrophilic and are more strongly hydrated [12]. This results in the formation of interactions between residual kosmotropic salts embedded in the multilayer and water that are highly favourable when compared to the ones with the more hydrophobic chaotropic salts, thus enhancing the hydrophilicity of the membranes, hence also contributing to the remarkable increase in water permeabilities.

### 4.4. Molecular weight cut off (MWCO)

To evaluate the size exclusion behaviour of the prepared membranes, MWCO measurements were performed (Fig. 8).

The findings obtained in Fig. 8 show that all the membranes prepared can retain solutes with a MW below 1200 kDa, with the majority of the membranes even having MWCO values well below 400 kDa. Furthermore, a clear odd-even effect is found for the membranes prepared with chaotropic salts (NaBr, MgCl₂, NH₄Cl, NaCl, LiCl). For those membranes the PDADMAC terminated layers have an MWCO much higher than the PSS terminated layers (striped bars in Fig. 8). The latter retain solutes with a MW lower than 350 Da and the trend follows the results observed for the water permeability (Fig. 7) following the same reasoning.

The membranes prepared with kosmotropic salts exhibit a MWCO below 310 Da for PDADMAC terminated layers and below 375 Da for PSS terminated layers. Remarkably, they simultaneously reach water permeabilities almost up to 6 times higher than their chaotropic counterparts (Fig. 7) without compromising and often even improving the solute rejection properties, regardless of the nature of the terminating layer. It is in fact, observed that the odd-even effect appears to level off after 4 bilayers guaranteeing quasi-constant performances in terms of both water permeability and MWCO (SI, Figs. S2 and S3), regardless the nature of the terminating layer. This is noteworthy as it can tremendously reduce membrane preparation time, notoriously lengthy [6,57],

![Fig. 7. Water permeability the membranes prepared with the different salts in the coating solution. Solid bars represent the values for PDADMAC terminated layers. Striped bars represent the values for PSS terminated layers.](image-url)
while still achieving good performances.

4.5. Salt retention

Salt retention measurements using MgSO$_4$, Na$_2$SO$_4$ and MgCl$_2$ were carried out as well (Fig. 9).

The retention of MgSO$_4$ (Fig. 9a) distinctly follows the same trend shown for the water permeability (Fig. 7) and MWCO (Fig. 8). Once again, the odd-even effect is clearly visible for the membranes prepared with chaotropic salts and results in retentions that reach values up to 90% for PSS terminated membranes (NH$_4$Cl membrane) and as low as 14% for PDADMAC terminated ones (NaCl membrane). Following the reasoning described earlier, PDADMAC terminated layers form more open, coiled structures and are subject to more severe swelling than PSS ones resulting in higher chain mobility thus, higher free volume. This translates into higher water permeability, higher MWCO and ultimately translates into lower size exclusion compromising the retention towards MgSO$_4$. Oppositely, the membranes prepared with kosmotropic salts ensure superior retention properties. The tight ionic linkages between the PEs resulting from higher intrinsic charge compensation and low
swelling guarantee high MgSO₄ retentions, which reach up to 95% ((NH₄)₂SO₄ as coating salt), and relatively constant performances regardless the nature of the terminating layer.

It is critical to acknowledge that the contribution of the salts used in this work is not limited to tuning the charge compensation mechanism (extrinsic or intrinsic) of the PEs. If that would be true and the impact of kosmotropic salts would result only in intrinsic charge compensation, the performances would be comparable to a membrane in which PDADMAC and PSS are coated in the absence of additional salt or at very low ionic strengths. This is in fact not accurate, as previous literature shows that the preparation of an LbL membrane with PDADMAC/PSS at a very low ionic strength (5 × 10⁻⁵ M NaCl and similar experimental conditions compared to this work) results in very thin multilayers that, despite showing outstanding water permeabilities, has poor rejection properties [11]. It follows that kosmotropic and chaotrope salts do influence the PEs charge compensation mechanism but most importantly, while still allowing for the formation of sufficiently thick layers to guarantee good salt rejections and MWCO, with consequences for the hydrophilicity and permeability of the membranes as well.

The retention towards Na₂SO₄ and MgCl₂ are very insightful to evaluate the specific relevance of charge exclusion (Donnan exclusion) or size exclusion effects on the retention behaviour of the prepared membranes. As seen in Fig. 9b and c, the retention towards Na₂SO₄ and towards MgCl₂ are almost perfectly symmetrical. As a matter of fact, Na₂SO₄ retention is moderate for the membranes prepared with chaotropic salts reaching a maximum of 38% for the PSS terminated layers for the membranes prepared with LiCl. On the contrary, the membranes prepared with kosmotropic salts attest in all cases a significant increment of Na₂SO₄ retention reaching even 97%. This is independent of the nature of the terminating layer, indicating an overall negatively charged nature of the multilayer assembly. Furthermore, this directly correlates with the findings and reasoning obtained with reflectometry (Fig. 5) as they show a higher mass adsorption of PSS compared to PDADMAC and to the zeta potential results (Fig. 6) showing significantly lower values for the membranes prepared with kosmotropic salts.

MgCl₂ retentions on the other hand, show exactly opposite behaviour: Membranes prepared with chaotropic salts show very high MgCl₂ retentions regardless of the nature of the terminating layer, while those prepared with kosmotropic salts show low retentions (Fig. 9c). The explanation to this is found in the reflectometry results for which the mass adsorption of PDADMAC is indeed higher when chaotropic salts are used in the coating stage (Fig. 5). This in turns gives rise to higher zeta potential values for the membranes prepared with chaotropic salts (Fig. 6) and ultimately results in higher retentions of MgCl₂. Unsurprisingly, better retentions for MgCl₂ are observed for the PSS terminated layers than for the PDADMAC ones. These layers show significantly higher MgSO₄ rejection and lower MWCO indicating that the two ion rejection mechanisms, size and charge exclusion, cooperatively work to achieve the obtained performances.

In a nutshell, the use of chaotropic salts in the LbL membrane coating stage results in the formation of preferential interactions between the anions of the salts (Br⁻, Cl⁻) and PDADMAC leading to its effective extrinsic charge compensation thus, formation of an open multilayer. This does not allow to achieve good MgSO₄ retentions but, due to the higher mass adsorption of the PC, delivers membranes with a significantly high surface charge that show excellent retentions towards MgCl₂. Kosmotropic salts instead, while promoting interactions between oppositely charged PEs leading to the formation of tight ionic linkages, hence notable MgSO₄ retention, allow for higher adsorption of PSS resulting in negatively charged membranes that show remarkable retention for Na₂SO₄.

Although both size and charge exclusion mechanisms play a role and determine the overall retention performances of the membranes prepared, the higher retentions found for MgCl₂/Na₂SO₄ compared to MgSO₄ clearly indicate the dominance of charge exclusion.

It is interesting to notice that the results obtained in this work are not influenced by the charged nature of the ions present in the coating solution: The chaotrope salt containing Mg²⁺ (MgCl₂) gives rise to similar performances as the salts containing a monovalent cation (NaBr, NH₄Cl, NaCl, LiCl). Similarly, the kosmotrope salt containing H₂PO₄⁻ gives rise to similar performances as the salts containing a divalent anion (MgSO₄, (NH₄)₂SO₄, Na₂SO₄).

Finally, even though the use of kosmotropic/chaotropic cations of the salts present in the coating solutions shows an impact on the adsorption behaviour of the PEs (Fig. 3), it reveals to be insufficient to give rise to significant differences in the membrane performances. The differences in water permeability, MWCO and salt retention between the membranes prepared in this work are to be ascribed mostly to the different kosmotropic/chaotropic nature of the ions in the salts present in the coating solution.

5. Conclusions

We systematically studied the effect of specific ion effects to tune the properties of layer-by-layer membranes of the PEs (polydiallyldimethylammonium chloride and polystyrene sodium sulfonate). NaBr, NH₄Cl, MgCl₂, NaCl, LiCl, MgSO₄, NaH₂PO₄, (NH₄)₂SO₄, Na₂SO₄ classified into kosmotropes and chaotropes were added to the PE coating solutions and membrane properties (i.e. mass adsorbed, zeta potential) and membrane performance (i.e. water permeability, MWCO, retention) were determined.

Chaotropic salts (NaBr, NH₄Cl, MgCl₂, NaCl, LiCl) promoted exponential growth of the multilayer and resulted into thick assemblies. This was justified with the formation of favourable interactions between the chaotrope anions with the chaotropic PDADMAC hence, strong extrinsic charge compensation and looping of the PC chains. This effect was reduced for PSS giving the less chaotropic nature of the cations in the salts and lower mass adsorption. This odd-even effect translated into high resistance of the multilayer as a whole and higher water permeability for PDADMAC terminated layers than PSS ones. Consequently, also the MWCO and MgSO₄ retention data follow the same trends. Higher adsorption of PDADMAC compared to PSS for the membranes prepared with chaotropes, resulted into membranes with positive surface charge allowing for good rejections of MgCl₂.

Kosmotropic salts (MgSO₄, NaH₂PO₄, (NH₄)₂SO₄, Na₂SO₄) interacted poorly with the PEs due to their different enthalpy of hydration. This allowed for more intrinsic charge compensation of the PDADMAC/ PSS charges and the formation of strong ionic linkages between them. It then resulted into much lower mass adsorption and delivered thin layers with a water permeability that was almost 6 times as high as the one of the membranes prepared with chaotropic salts. This without compromising the size exclusion behaviour of the membranes which showed a MWCO as low as 310 Da and a MgSO₄ that reached up to 95%. The highly negative nature of the membranes prepared with kosmotropic salts allowed to obtain rejections towards Na₂SO₄ that went up to 97%. Most importantly, these performances were quasi-stable after depositing only 4 PE bilayers, regardless of the nature of the terminating layer, demonstrating the potential of this approach. As a matter of fact, even though it would need further testing this approach could potentially translate into easier upscaling and wider application possibilities of the technology with significant shortening of the coating times.

Credit author statement

Anna Casimiro contributed to conceptualization, methodology, validation, formal analysis, investigation, writing-original draft and review & editing, and visualization. Cees Weijers contributed to validation, formal analysis and investigation. Danielle Scheepers contributed to methodology and formal analysis. Zandrie Borneman contributed to supervision, writing review & editing and project administration. Kitty Nijmeijer performed supervision, writing review & editing, project administration, and funding acquisition.
Declaration of competing interest

The 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.

Acknowledgements

This research was part of the research program START-UP with project number 740.018.005, which is financed by the Dutch Organization for Scientific Research (NWO). The authors want to thank Marjolein Boom from the Eindhoven University of Technology for the preparation and characterization of the membranes with MgCl₂, MgSO₄ and Na₂SO₄.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.memsci.2023.121446.

References


