Ion specific effects on aqueous phase separation of responsive copolymers for sustainable membranes

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GRAPHICAL ABSTRACT

Tuning Aqueous Phase Separation with salts

LlI*: Na*, NH4+, Mg**, Ca**, Cl-, NO3-, SO4-**

Cross-section
Top surface

ABSTRACT

Hypothesis: Salt identity and concentration affects the preparation of membranes via the aqueous phase separation approach. The phase inversion process and morphology of the resultant membranes is expected to vary as function of these two parameters.

Experiments: Polymeric membranes based on the responsive copolymer polystyrene-alt-maleic acid (PSaMA) are prepared using the aqueous phase separation approach and the influence of salt identity (Na2SO4, LiCl, NaCl, NaNO3, NH4Cl, MgCl2, CaCl2) and concentration on resultant membrane morphology and separation performance is investigated. Complementary stability experiments of PSaMA solutions are performed to help understand the intricate aqueous phase separation process.

Findings: Specific ion effects are observed during membrane formation by the aqueous phase separation approach. At equal ionic strengths, Na2SO4 and LiCl lead to the formation of more open membrane structures compared to NaCl, NaNO3, NH4Cl, MgCl2, CaCl2, while CaCl2 results in membranes with dense top layers. These ion-specific effects are likely caused by a combination of ion mobility and interaction potential between the ion and the polyelectrolyte. Overall, from this work it becomes clear that salt identity and concentration are key parameters in the APS process, and they can be optimised to tune membrane structure from open microfiltration to dense nanofiltration membranes.

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1. Introduction

In a world that strives for improved sustainability, membranes play an important role in optimising separation processes because
they are often more energy efficient than conventional techniques like distillation or extraction [1,2]. A lot of current research is focused on improving membrane performance, yet a very important issue that is often overlooked is the need for sustainability within the membrane fabrication process [3]. The production of polymeric membranes is most commonly based on the non-solvent induced phase separation (NIPS) method, which uses large quantities of reprotoxic organic solvents such as N-methyl pyrrolidinone (NMP) and dimethylformamide (DMF) [4]. Finding suitable alternatives to these solvents is becoming a pressing issue as the European Union is restricting the use of NMP from May 2020 [5]. Indeed in recent years, alternative membrane fabrication processes that use more benign solvents have been proposed; including ones that use ethyl lactate, ionic liquids, supercritical CO2 and even water [6–11]. The complete replacement of toxic solvents with greener alternatives for membrane production is still in its infancy, however in several cases, membranes prepared using these greener solvents have achieved performances comparable to those produced by the classical NIPS approach.

Among these alternative methods, Aqueous Phase Separation (APS) stands out because of its versatility and its lack of reliance on organic solvents [11–14]. As of now there exist three different APS approaches: 1. Where a single pH-responsive, weak polyelectrolyte is dissolved in water in its charged state and precipitated using a pH switch; [11,12] 2. Where a weak polyelectrolyte is initially mixed with an oppositely charged strong polyelectrolyte at a pH where the weak polyelectrolyte is uncharged, and then a switch in pH induces complexation between the two polymers and thus phase separation; [13] and 3. Where two oppositely charged strong polyelectrolytes are mixed at high salt concentration, which prevents complexation, and switching to low salinity induces complexation of the polymers. [14] The main advantage of all three APS methods is that it is possible to produce membranes in a more sustainable and environmental friendly fashion without the reliance on toxic solvents such as NMP and DMF.

Apart from the solvent and polymers used, APS is very similar to NIPS. In both cases the polymer(s) are dissolved in a solvent where the polymer–solvent interactions are favourable and the resultant solution is homogeneous. When a cast film of this polymer solution is submerged into a non-solvent bath, a solvent exchange occurs and this results in unfavourable polymer–solvent interactions causing the phase separation. As with NIPS, a low driving force for phase separation results in more symmetrical, open membrane structures and a high driving force results in more asymmetric membranes with denser top layers. When considering APS with a single acidic polyelectrolyte, H2O can be seen as the solvent and H3O+ as the non-solvent. At a pH > pk a, the polymer is charged and polymer–solvent interactions are favourable resulting in a stable single-phase solution. An important difference between this APS system and NIPS is that the introduction of the non-solvent changes the polymer itself instead of changing the solvent–polymer interactions. Here, H3O+ protonates the weakly anionic polymer which causes it to lose its negative charge. The reduction in charge makes it thermodynamically unfavourable for the polymer to remain in solution as polymer–polymer interactions are now more favourable than polymer-solution interactions and thus the polymer precipitates. A very important kinetic parameter of this system is the rate at which the polymer loses its charge. Using a larger concentration of H3O+ results in a larger driving force to protonate and therefore precipitate the polymer and vice versa. This can be compared to the solvent to non-solvent ratio in NIPS, where the addition of solvent to the coagulation bath can be used to slow down the kinetics of the phase separation.

Since APS is water-based and relies on polyelectrolytes it can readily make use of additional tuning parameters that are rarely used in conventional NIPS, the salt type and concentration. It is well-established that the behaviour of polyelectrolytes in solution can be controlled by salt concentration. [15] Moreover, it has been known for a long time how specific salts (or ions) can precipitate/stabilise polyelectrolytes from/in solution (‘salting-out’ and ‘salting-in’, respectively) [16–17] i.e. specific ion effects, but to the best of our knowledge this effect has yet to be studied in the context of synthetic membrane formation. From the perspective of well-defined colloidal systems [18] such as negatively charged silver iodide sols [19] and anionic polystyrene latex particles, [20–22] individual cations and anions can be ordered from those that have the greatest salting-out effect (i.e. lowest critical coagulation concentration, CCC, for the colloidal solutions) to those that have the least (i.e. highest CCC). This leads to the following series for cations: Ca2+ > Mg2+ > NH4+ > K+ > Na+ > Li+, and anions: SO42− > F− > Cl− > NO3− > SCN−. Sequences of such data are known as lyotropic series or Hofmeister series. Throughout the literature, the position of individual ions in these series is variable, for example the position of NH4+ can shift due to its hydrogen-bonding capacity. [23] Moreover, completely inverted (or reversed) series are found depending on the given experiment and experimental conditions such as pH. [24,25] Ionic strength/concentration, [26] solute/surface charge and polarity, [27] and temperature; [28] as elegantly discussed in the following review articles. [29,30] Beyond these effects, the physical properties of ions (e.g. ionic size, polarizability, hydration strength and 'hydrophobicity') are also important. [31] At present, the scientific community is yet to uncover the fundamental origins of specific ion effects, but seemingly the general consensus is now that they result from the complex interplay of a number of interactions in solution i.e. ion–solvent, ion–solute, ion–ion, solute–solvent, solute–solute, and solvent–solvent interactions [32].

In this work, the focus lies on studying the influence that different types of salt and concentrations thereof have on the formation of polymeric membranes prepared using polystyrene-alt-maleic acid (PSaMA). This copolymer is used since it contains both responsive, maleic acid, and unresponsive, styrene, monomers which allows for the preparation of mechanically stable membranes as shown in our previous work. [11] The ion specific effects of different mono- and divalent salts on membrane formation will be systematically evaluated at different concentrations. As PSaMA is a polyanion it is expected that cations will primarily have a more significant influence on the phase inversion behaviour. Divalent cations are expected to have a stronger effect due to their potential to form ionic crosslinks, which may increase polymer–polymer interactions and therefore accelerate the phase separation process. Moreover, an increase in salt concentration will increase charge screening and therefore reduce repulsion between the negative charges of the polymers. By investigating how salt affects the phase separation, additional control over membrane morphology can be achieved which in turn leads to membranes with improved performance.

### 2. Experimental section

**Poly(styrene–alt–maleic acid)** sodium salt solution 13% (Mw 350,000 g mol⁻¹, PSaMA), polyethylene glycol (Mw 200 g mol⁻¹, PEG 200; Mw 400 g mol⁻¹, PEG 400; Mw 600 g mol⁻¹, PEG 600; Mw 1500 g mol⁻¹, PEG 1500; Mw 2000 g mol⁻¹, PEG 2000), polyethyleneimine, branched (Mw 600 g mol⁻¹, PEl 600) were purchased from Sigma Aldrich. N–(3-Dimethylaminopropyl)–N–ethyl carbodiimide hydrochloride (EDC), N–Hydroxysuccinimide (NHS), magnesium sulfate, magnesium chloride, sodium sulfate, sodium dodecyl sulfate (SDS), glacial acetic acid, and hydrochloric acid 37% were purchased from Sigma Aldrich. Ethanol 100% technical grade, was purchased from Boom B.V. N–hexane 99% was bought...
from Acros organics. Sodium chloride (Sanal® P) was purchased from AkzoNobel. To prepare coagulation baths, deionized water (DI, 1.0 μS cm⁻¹) was used and Milli-Q water (Millipore, 0.6 μS cm⁻¹) was used in the preparation of PSaMA solutions. The received PSaMA solution (Sigma Aldrich) was dried for 16 h at 100 °C and used without further purification. Other chemicals were used as received.

2.1. Turbidity experiments

Turbidity measurements were performed using a Turb® 430 IR – WTW portable turbidity meter. Solutions were prepared directly in the cuvettes (d: 25 mm, h: 40 mm) by mixing the salt (0.1–1 M ionic strength) into the polymer solution. After a homogenous solution was obtained, a vacuum was applied to remove air bubbles and then the solution was left for at least 12 h. Turbidity is measured in formazin nephelometric units (FNU) which is based on scattered light from dispersed colloidal particles of a formazin standard (where the particles have a turbidity of 1 FNU and are made in water by mixing 1.25 mg L⁻¹ of hydrazine sulfate with 12.5 mg L⁻¹ of hexamethylenetetramine) [33].

2.2. Membrane preparation

The membranes were prepared in similar fashion to our previous work with the vital details reported below [11]. To prepare the polymer casting solutions PSaMA (20% w/v) was dissolved in water (40% v/v) with acetic acid (40% v/v). After a homogenous solution was obtained via stirring, it was filtered through a Bekart 25 μm Bekipor ST25 AL 3 steel filter. For degassing, the solution was allowed to rest for at least 24 h. The polymer solution was cast on a glass substrate using a steel casting knife with a 0.3 mm gap height. The film was then submerged in an acidic coagulation bath containing 2 M acetic acid, 0.04 M HCl, and either one of the following salts; NH₄Cl, NaCl, LiCl, NaNO₃, Na₂SO₄, MgCl₂, CaCl₂ at 100 °C. The film was then submerged in an acidic coagulation bath (25 μm Bekipor ST25 AL 3 steel filter). For degassing, the solution was allowed to rest for at least 24 h. The polymer solution was cast on a glass substrate using a steel casting knife with a 0.3 mm gap height. The film was then submerged in an acidic coagulation bath containing 2 M acetic acid, 0.04 M HCl, and either one of the following salts; NH₄Cl, NaCl, LiCl, NaNO₃, Na₂SO₄, MgCl₂, CaCl₂ at varying ionic strengths. Cast films were left in the coagulation bath for 5 min followed by three washing steps of 30 min using 0.1 M HCl. Crosslinking of the membranes was achieved with an aqueous carbodiimide based crosslinking method with branched low molecular weight PEI using the same method as in our previous work [11,34]. Post crosslinking the membranes were rinsed with and stored in DI water.

2.3. Membrane performance tests

Membrane performance was studied with dead-end filtration cells using a pressurized feed vessel following the same protocol as our previous work. [11] The pure water permeability of the membranes (surface area of 38 mm²) as well as their retention of oil droplets, salt and small molecules was measured. Details of these measurements can be found in the Supporting Information.

2.4. Scanning electron microscopy (SEM)

Membrane samples for SEM analysis were prepared after the membranes were washed twice in ethanol and twice in n-hexane for 30 min and then dried. The samples were fractured after immersion in liquid nitrogen and subsequently mounted on a sample holder. The samples were stored in a vacuum oven at 30 °C for at least 4 h, after which 10 nm chromium was sputtered onto the samples using a Quorum Q150T ES. Imaging was performed using Jeol JSM–6010LA scanning electron microscope.

3. Results and discussion

In this work, the influence of different salts on the precipitation of PSaMA for sustainable membrane production is investigated in three parts: 1. Ion specific effects were studied in a model system using turbidity measurements; 2. It is shown that by using different types of salt and/or salt concentrations in the coagulation bath, different membrane structures can be obtained; 3. The separation performance of a selection of the membranes prepared is investigated.

3.1. Ion specific effects on turbidity of PSaMA solutions.

To understand the influence that different types of salt have on the solution stability and precipitation of PSaMA, it is important to understand how the different salts interact with PSaMA. This is achieved by measuring the turbidity of PSaMA solutions containing different types and ionic strengths of added salt. The turbidity of the solutions is studied as it provides a clear indication of which salts strongly induce phase separation and which salts do not, which is akin to the salting-out and salting-in effects first described by Hofmeister for salts and proteins. [35] The turbidity was measured for a series of PSaMA solutions prepared with different salt concentrations using ionic strengths ranging from 0 M to 1 M with the results presented in Fig. 1a. To allow for comparison between the mono- and divalent ions, molar ionic strength is used throughout this study. Due to ease of preparation a 13% w/v PSaMA solution is studied in Fig. 1a. The general trend is that when more salt is added, the turbidity increases and this signifies phase separation. Significant differences are observed depending on the type of salt. The large turbidity increase seen for divalent cations was expected as these salts can most likely form ionic crosslinks between the polymer chains by coordinating with two different carboxylate units. The different monovalent cations have a lower, but nonetheless distinct effect on solution turbidity as the ionic strength increases. For cations, the trend observed in Fig. 1a directly follows the stability of negatively charged carboxyl-functionalised polystyrene latex particles in water. [20] i.e. the salting-out efficiency of cations on PSaMA is Ca²⁺ > Na⁺ > NH₄⁺ > Li⁺ (Li⁺ was not studied by López-León et al., but it is typically found close to Na⁺ in the lyotropic/Hofmeister series). For the anions, the salting-out effect on PSaMA is greater in Cl⁻ than in NO₃⁻, which follows the trend observed by López-León et al. [20] However, the behaviour of PSaMA in the presence SO₄²⁻ (i.e. little to no salting out effect) is different and is likely due to the use of ionic strength in our study rather than molar concentration for the divalent salt.

Fig. 1a clearly shows that dramatic ion specific effects are present with PSaMA in solution. This indicates that the precipitation behaviour of PSaMA will be influenced by different types and concentrations of salt. Fig. 1b shows, as expected, that besides salt concentration the polymer concentration also significantly affects solution turbidity. At 7% w/v PSaMA it is observed that the turbidity is independent of NaCl concentration, while at 20% w/v the dependency is increased significantly. This is as expected as at higher polymer concentrations there are more interactions between the polymer chains. For 20% w/v polymer, it is also observed that even at 0 M salt the solution is already quite turbid, indicating that even without any additives PSaMA undergoes partial phase separation. In the coming sections, it will be shown that by tuning the salt type and concentration it is possible to control the phase separation process and prepare different types of membrane structures.

3.2. Ion specific effects on membrane formation

To investigate ion specific effects on membrane formation, membranes were prepared using a 20% w/v PSaMA solution with...
40% v/v acetic acid precipitated in a coagulation bath containing 2 M acetic acid, 0.1 M NaCl and 0.04 M HCl. These conditions were optimized in our earlier work to prepare microfiltration membranes with a good separation performance. [11] Herein, to investigate the influence of salt type the NaCl in the coagulation bath is substituted by 0.1 M ionic strength of Na2SO4, NaN03, LiCl, NH4Cl, MgCl2 or CaCl2. As with the turbidity experiment in Fig. 1a, equal ionic strengths were used instead of equimolar concentrations to allow comparison between the divalent and the monovalent ions. In Fig. 2, significantly different membrane structures are observed when different ions are present in the coagulation bath. Overall, three distinct types of membrane structures are observed. Firstly, Na2SO4 and LiCl lead to the formation of a very open symmetric structures without distinct top layers. With MgCl2, NaN03, NH4Cl, and NaCl, the structures are also open, but now distinct porous top layers are observed. When CaCl2 is used in the coagulation bath, the resultant structure is asymmetric with macrovoids in the support structure and the film has a dense top layer with a significant amount of pin hole defects.

A more open structure results from slower precipitation kinetics and can be linked to how the ions in the coagulation bath interact with PSaMA. Conversely, faster precipitation results in more dense structures. The ions that lead to longer precipitation times (i.e. slower precipitation kinetics) can be considered as having a salting-in effect (or a minimal salting-out effect) on the anionic polyelectrolyte. While, ions that lead to more rapid precipitation of the polyelectrolyte can be thought of as having a salting-out effect. Based on the SEM images, when the ions are ordered from those that have the strongest salting-out effect to the least, the following series are obtained for cations: Ca2+ > Mg2+ > NH4+ > Li+, and anions: Cl− > NO3− > SO42−. It is difficult to directly link these series to the lyotropic/Hofmeister series since it follows neither the direct nor indirect series, indicating that there is likely a complex interplay of a number of factors. Differences in the charge density, polarizability, hydration strength and ‘hydrophobicity’ of the ions all likely play a role in how they interact with PSaMA and how PSaMA interacts with water. [31]

Since PSaMA is a copolymer with both anionic and neutral monomers it is expected that ions will interact differently with both monomers. For the hydrophobic styrene monomers, larger and more weakly hydrated ions (e.g. NH4+) are expected to have a stronger interaction than smaller more strongly hydrated ions (e.g. Li+). [36–37] While for the ionisable maleic acid monomer one might expect very different ion–polymer interactions. For example, Schwierz et al. demonstrated that Li+ has a high affinity for carboxylic acid groups and thus Li+ may be able stabilise the PSaMA in solution, which may explain why Li+ gives more open membrane structures. [25] Mg2+ and Ca2+ result in vastly different membrane structures, but this is not predicted when considering the lyotropic/Hofmeister series. This is likely due to the high polymer concentrations used in this current study, which allows for the formation of substantial interpolymer ionic crosslinking. Ca2+ leads to more denser structures than Mg2+ indicating that Ca2+ has a much stronger salting-out effect than Mg2+, possibly caused by a stronger affinity of Ca2+ to carboxylic acid groups of PSaMA than Mg2+. In support of this hypothesis, it is known that Ca2+ promotes gelation of alginate through ionic crosslinking of carboxylic acid groups, while Mg2+ does not. [38–39] One should also take into account that ion specific effects are pH dependent [24–25] and therefore will change during the phase separation process.

When comparing the membrane structures observed with SEM (Fig. 2) to the turbidity data (Fig. 1) the trends are very similar except for Li+ and Mg2+, with these differences discussed in detail above. One very important difference between the two experiments is that during membrane formation the salt is present in the coagulation bath and not the polymer solution like in the turbidity measurements. Therefore, the salt must diffuse into the precipitating polymer film to be able to interact with the polyelectrolyte (PSaMA); thus the diffusion coefficients of the ions becomes an important parameter to consider during membrane preparation while it is not as significant for the turbidity experiment. In Table 1, the diffusion coefficients [40] are listed for the ions and salts used in this study. The relatively low diffusion of LiCl in comparison to NaCl and NH4Cl can be a possible explanation as to why a more open structure is formed when LiCl is used. Even though MgCl2 has a strong effect on the phase separation as seen in Fig. 1a, MgCl2 also has a low mobility in the coagulation bath, which may explain why the resultant membrane has an open structure. However, this diffusion argument does not explain the structure obtained when CaCl2 is used. Based on the relatively low diffusion coefficient of CaCl2 an open structure would be expected, yet an asymmetric structure with a dense top layer is observed. Most likely the strong affinity of Ca2+ to carboxylate groups and its ability to ionically crosslink PSaMA means that for Ca2+ a dense top layer is rapidly formed when the film of PSaMA is exposed to the coagulation bath that in turn hinders the diffusion of acetic and hydrochloric acid into and out of the precipitating film, resulting in the formation of macrovoid defects. This
shows that the phase separation is a complex process in which ion specific effects and mobilities clearly play an important role in determining the structure of the membrane even at concentrations as low as 0.1 M ionic strength.

In the turbidity experiment of Fig. 1, it is observed that at higher ionic strengths the ion specific effects become more pronounced. To study this concentration effect on membrane formation, membranes were prepared at 0.3 M and 0.9 M ionic strength for each of the salts. In Fig. 3, already at 0.3 M ionic strength, the structures of the precipitated films are drastically different from the 0.1 M films. For all conditions at 0.3 M, membranes with a denser top layers are formed compared to the mostly open structures observed in Fig. 2. Such behaviour can be attributed to the increased charge screening which results in a reduction of the electrostatic repulsion between the carboxylate groups of PSA. This in turn leads to the more rapid onset of phase inversion, which favours the formation of membranes with denser top layers. The structures prepared with 0.3 M ionic strength of Na2SO4 and LiCl now have dense top layers, but they have multiple pinhole defects. The membrane prepared with LiCl has less pinhole defects but the top layer delaminates from the support structure. For all other salts, asymmetric structures are observed with thin dense top layers and macrovoids in the support structures. From the SEM images, the membrane prepared with 0.3 M ionic strength CaCl2 appears to be the only membrane without defects in the top layer. For the other salts the macrovoids are situated very close to the top layer resulting in many pinhole defects.

Further increases in the ionic strength of salt in the coagulation bath to 0.9 M ionic strength results in further densification of the top layer as observed in Fig. 4. All structures are now asymmetric with macrovoids including the ones prepared with Na2SO4 and LiCl, although they still have multiple defects in the top layer. The membranes prepared with MgCl2 and NaNO3 also have a significant number of defects in the top layer. When 0.9 M ionic strength of NH4Cl, NaCl, and CaCl2 are used in the coagulation bath, no defects are observed in the top layer. Indicating that these films may have interesting membrane properties. When comparing the SEM images in Figs. 2–4, a very clear trend is observed; where increases in salt concentration lead to denser top layers and more asymmetric structures. In addition, significant ion specific effects are observed at each concentration, salts like LiCl and Na2SO4 are very suitable to prepare open structures, while CaCl2 can be used even at low concentrations to prepare membranes with dense separation layers. From the results discussed above, it appears that the affinity of ions to the polymer as well as the mobility of the ions in the coagulation bath both play very important roles. For instance, Ca2+ ions that can likely form strong ionic crosslinks with the polymer, give rise to denser membrane structures, while Li+ may be able to better stabilise the polymer in solution resulting in more open membrane structures. Overall, this data shows that salt type and concentration provide two additional control parameters that can be used to fine tune the structure of membranes made using the Aqueous Phase Separation process.

### Table 1

| Ion      | D (10^{-5} cm² s⁻¹) | Salt     | D (10^{-5} cm² s⁻¹) |
|----------|----------------------|----------|----------------------|
| H⁺       | 9.31                 | HCl      | 3.34                 |
| NH₄⁺     | 1.96                 | NH₄Cl    | 1.99                 |
| Na⁺      | 1.33                 | NaCl     | 1.61                 |
| Li⁺      | 1.03                 | NaNO₃    | 1.57                 |
| Ca²⁺     | 0.79                 | LiCl     | 1.37                 |
| Mg²⁺     | 0.71                 | CaCl₂    | 1.34                 |
| Cl⁻      | 2.03                 | MgCl₂    | 1.25                 |
| NO₃⁻     | 1.90                 | Na₂SO₄   | 1.23                 |
| CH₃COO⁻  | 1.09                 |          |                      |
| SO₄²⁻    | 1.07                 |          |                      |

Fig. 2. SEM images of cross sections and top surfaces of membranes prepared in a coagulation bath with 2 M acetic acid, 0.04 M HCl and 0.1 M ionic strength of Na₂SO₄, LiCl, MgCl₂, NaNO₃, NH₄Cl, NaCl, and CaCl₂ using a 20% w/v PSA, 40% v/v acetic acid polymer casting solution.
3.3. Membrane performance

To investigate the performance of the membranes produced using the different salts, pure water permeability and retention measurements were performed. In Fig. 5, the pure water permeability and oil droplet retention is displayed of the membranes prepared with 0.1 M ionic strength of Na2SO4, LiCl, MgCl2, NaNO3, NH4Cl, NaCl, and CaCl2 using a 20% w/v PSamA, 40% v/v acetic acid polymer casting solution.

3.3. Membrane performance

To investigate the performance of the membranes produced using the different salts, pure water permeability and retention measurements were performed. In Fig. 5, the pure water permeability and oil droplet retention is displayed of the membranes prepared with 0.1 M ionic strength of Na2SO4, LiCl, MgCl2, NaNO3, NH4Cl, NaCl, and CaCl2 using a 20% w/v PSamA, 40% v/v acetic acid polymer casting solution.
the membranes prepared with Na₂SO₄ and LiCl show the lowest permeability while having the most open structure. A possible explanation is that since the support structure appears to have a smaller pore size compared to the other membranes it has a higher resistance. For the membrane prepared with Na₂SO₄ it is also observed that the top structure partially collapses under applied water pressure and this structural compaction reduced the water permeability as seen in Figure S1. The membranes prepared with MgCl₂, NaNO₃, NH₄Cl, and NaCl have similar water permeabilities, but the NH₄Cl membranes showed quite some deviation in the measured permeability, shown by the large error bar. The large deviations in permeability between the measured samples (at least 6) indicates that some of the membranes prepared with NH₄Cl have defects in the selective layer which can greatly enhance the flux, but always in an irreproducible way. This was confirmed by the SEM images, as some of the membranes had multiple defects resulting in a locally increased pore size and porosity of the selective layer. Surprisingly, even though the top layer of the 0.1 M CaCl₂ membrane is mostly dense (by SEM), it has much the same water permeability as the other 0.1 M membranes. Here, for the 0.1 M CaCl₂ membrane, it is expected that the water permeability is completely dominated by the many defects present in the selective layer which would also explain the large standard deviation for this system. For the oil droplet retention, all membranes besides the one prepared with CaCl₂ have > 99% retention which is as expected since all pores observed with SEM imaging are significantly smaller than the size of the oil droplets. The much lower retention for the membrane prepared with CaCl₂ is likely because of the defects in the top layer of which some are larger than the size of the oil droplets. This shows that all other membranes have no major defects which would otherwise affect their microfiltration performance.

Of the membranes prepared at higher salt concentrations, those prepared with 0.3 M (Fig. 3) and 0.9 M (Fig. 4) ionic strength of CaCl₂ were investigated further with water permeability and salt retention measurements. As seen in Fig. 6 the water permeability is low for both membranes, which is not unexpected as these membranes have a dense top layers. Similar membrane materials in our previous work also had a low water permeabilities. [11] The MgSO₄ retention of the membrane prepared with 0.3 M ionic strength of CaCl₂ was low. This indicates that the membrane most likely has very small defects in the top surface, which is why this membrane was not investigated further. The membrane prepared with 0.9 M ionic strength CaCl₂ displayed a slightly lower water permeability, but an excellent MgSO₄ retention that is on par with nanofiltration membranes produced by conventional phase inversion methods. [42–43] The retention of other salts was measured to acquire an understanding of the predominant separation mechanism. When comparing the retention of Na₂SO₄ and MgCl₂ it is observed that Na₂SO₄ is retained more and this is most likely due to the negative charge of PSAmA membranes. Ion size and valency also plays an important role as the small and monovalent NaCl is retained the least. To estimate the ability of the membrane to retain organic molecules, molecular weight cut-off measurements where performed using small polyethylene glycol (PEG) molecules. As seen in Figure S2, a molecular weight cut-off of 230 ± 30 g mol⁻¹ was measured, which confirms that this membrane is a nanofiltration type membrane. This shows that with salt type and concentration the aqueous phase separation can be controlled to produce both open and dense membranes in a way that is simply not possible in conventional NIPS.

4. Conclusions

Our previous studies highlight the promise of aqueous phase separation as a more sustainable approach to preparing polymeric membranes [11,12]. In this current work, it is shown that the precipitation of a weak polyelectrolyte into different porous membrane materials is strongly dependent on salt identity and salt concentration. Initial polymer stability studies indicated that substantial specific ion and concentration effects would be present during membrane formation by phase inversion. Divalent cations strongly promoted the precipitation of the responsive copolymer PSAmA, which was likely due to ionic crosslinking effects. The impact of the different salts on aqueous phase separation and resultant membrane structure was systematically investigated and it was found that at equal ionic strengths, Na₂SO₄ and LiCl gave more open structures compared to MgCl₂, NH₄Cl, NaNO₃, and NaCl. CaCl₂ on the other hand led to denser membrane structures. At higher salt concentrations, the influence of salt identity followed the same order as at lower concentrations, but all the membranes...
were denser. Overall, ion mobility and the affinity of the ions to polymer are both expected to play an important role in how ions affect the phase inversion and thus resultant membrane morphology. Divalent cations are of particular interest as they densify the membrane structure most likely due to ionic crosslinking interactions during the precipitation.

The open microfiltration membranes exhibited high oil droplet retentions with water permeability dependent on the type of salt used in the coagulation bath during phase inversion. The dense top layer nanofiltration membranes prepared with 0.9 M ionic strength CaCl₂ exhibited excellent retentions towards divalent ions, good retention towards NaCl, and a low MWCO value. The performance of these membranes is the same as those prepared in our previous work, [11] and in addition their ion retentions and MWCO is on par with commercial membranes prepared using conventional NIPS methods albeit with lower water permeability [44,45]. One needs to keep in mind that the state-of-the-art NIPS process has now been researched for approximately 60 years. The significant advantage of this alternative APS process is that it offers a more sustainable route to membrane preparation. Overall, this work demonstrates for the first time that the salt concentration and additional control parameters that can be used in the APS approach to control membrane morphology and performance in a way that is often not possible in conventional NIPS. Additional optimization remains possible through changes in both the polymer casting solution and coagulation conditions, which we expect will lead to membranes with higher water permeability and further improved ion and molecule retentions.

CRediT authorship contribution statement

Wouter M. Nielen: Conceptualization, Validation, Formal analysis, Investigation, Writing - original draft, Writing - review & editing. Joshua D. Willott: Conceptualization, Writing - review & editing, Supervision. Zephaniah M. Esguerra: Validation, Formal analysis, Investigation, Writing - original draft. Wiebe M. Vos: Conceptualization, Writing - review & editing, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declared that there is no conflict of interest.

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Appendix A. Supplementary material

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