On the influence of salt concentration on the transport properties of reverse osmosis membranes in high pressure and high recovery desalination
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Abstract

In this work, we investigate the effect of varying the concentration of sodium chloride up to 70 g.L\textsuperscript{-1} - equivalent to a recovery of approximately 50\% in seawater desalination- on the transport properties of different reverse osmosis membranes. The study was performed using five commercial thin film composite (TFC) membranes and an analogue TFC membrane fabricated via the interfacial reaction of m-phenylenediamine and trimesoyl chloride. The surface properties of the membranes as measured by atomic force microscopy (AFM), zeta potential, and X-ray photoelectron spectroscopy (XPS) are presented. The solution diffusion model coupled with film theory was used to calculate the permeance of water and salt through the membranes, to account for the effect of concentration polarisation. The mass transfer coefficient in the test cells was estimated independently using the dissolution rate of benzoic acid; and was found to be approximately $1 \times 10^{-4}$ m.s\textsuperscript{-1}. A linear reduction in salt permeance was observed in some of the RO membranes, while it remained constant for other membranes, including the analogue membrane. All the tested membranes maintained constant water permeance below 45 g.L\textsuperscript{-1}NaCl. However, when the salt concentration at the membrane surface exceeded 45 g.L\textsuperscript{-1}, water permeance either increased, remained constant or decreased. The results demonstrate the dependence of water and salt transport on the concentration of sodium chloride at the membrane surface.

Keywords: Reverse Osmosis, Solution Diffusion Model, Swelling, Salt Permeance, Water Permeance

1. Introduction

Thin film composite (TFC) membranes formed via the interfacial polymerisation of m-phenylenediamine (MPD) and trimesoyl chloride (TMC) on a polysulfone or polyethersulfone ultrafiltration support are the most widely used membranes in water treatment and desalination. This is due to the reliability and relatively low-cost of the interfacial polymerisation technique in producing membranes with excellent separation properties and a wide variety of surface properties \cite{1}. This enables the utilisation of TFCs in reverse osmosis water desalination systems with feed solutions ranging from low-salinity fresh and brackish water ($\sim$2-10 g.L\textsuperscript{-1} NaCl) to high- salinity seawater ($\sim$35 g.L\textsuperscript{-1} NaCl). Since, it is common to operate RO plants with overall recoveries around 50\% \cite{2}, the membrane elements in a seawater reverse osmosis (SWRO) plant are subjected to salt concentrations in the feed between 35 to 70 g.L\textsuperscript{-1} from the entry point until the solution exits the RO spiral wound elements.

Bartels et al. studied the effect of increasing the salt concentration in the feed up to 12 g.L\textsuperscript{-1} on commercial RO membranes \cite{3}. The salt passage through the membranes was shown to be dependent on the feed concentration, which was attributed to the effect of membrane surface charge on the strength of Donnan potential at low salinity \cite{3}. In their work, \cite{4}, Yasuda et al. studied the effect of increasing the concentration of sodium chloride in the feed up to 80 g.L\textsuperscript{-1} on the salt diffusion and partition coefficients in two different types of cellulose acetate (CA) membranes
and a hydroxypropyl methacrylate (HPMA) membrane, formed by non-solvent induced phase inversion, and showed that changing the concentration of the feed solution led to an increase in the diffusion and partition coefficients for the CA membranes and a reduction in the HPMA membrane. Mukherjee and SenGupta used available data in literature for thin film composite membranes, which includes membrane coupons and modules tested up to 0.88 M (51.4 g.L\(^{-1}\) NaCl) to show that the solute followed a coupled-transport mechanism, where individual ions partition into the membrane surface and diffuse through the active layer to the permeate side, even at higher concentrations [5].

Although significant advances have been reported in membrane transport models [6], the effect of feed concentration on the transport properties of salt and water is usually neglected. Furthermore, reported studies in literature focus on the performance of the membranes in the brackish water range (up to 20 g.L\(^{-1}\) NaCl) [7]. The available data for RO membranes in high recovery applications are usually limited to averaged values of salt and water fluxes at set operating conditions, or to a limited range of membranes [8-10]. The aim of this study is to provide deeper insight into the behaviour of several commercial RO membranes, as the concentration of sodium chloride in the feed is increased systematically up to 70 g.L\(^{-1}\). Since the fabrication process of commercial membranes is undisclosed, the transport properties of our analogue membrane, fabricated via the interfacial polymerisation of MPD and TMC, were also investigated to determine the impact of the chemical structure of the membrane on its separation properties. The mass transfer coefficient in the crossflow filtration cells was independently estimated via the rate of dissolution of benzoic acid, and data analysis was performed using the solution diffusion model combined with film theory, to take account for the influence of concentration polarisation on the observed permeation rates.

2. Theoretical background

![Figure 1](image_url)

**Figure 1.** (a) Depiction of the forces driving transport phenomena across the membrane, as hypothesised by the solution diffusion model. (b) Depiction of mass transfer limited membrane transport according to thin-film theory.

### 2.1. Solution diffusion model

In this work, the solution diffusion model was used to analyse the data obtained experimentally, which is widely accepted in describing transport phenomena in dense membranes, such as those employed in RO [6, 11]. Figure 1a shows the basic assumptions of the model regarding the driving forces affecting the transport across the separating layer of the membranes, where diffusion of permeating species is assumed to be the slowest step in the transport process. It is assumed that
only the separating layer influences transport; resistances in the support layer and nonwoven are assumed negligible, in line with common practice for RO simulations. Additionally, it is assumed that no pressure drop occurs through the separating layer of the membrane and an abrupt pressure drop occur in the layer of the membrane immediately adjacent to the low pressure side i.e. the permeate side. The governing equations of the solution diffusion model applied to reverse osmosis can be written as [11]:

\[
J_w = B_w \times (\Delta P - \Delta \Pi)
\]

Equation 1

Where

\[
B_w = \frac{D_w^m \kappa_w c_{w,x=0} \nu_w}{R_g T l}
\]

Equation 2

\[
J_s = B_s \times (c_{s,x=0} - c_{s,p})
\]

Equation 3

Where

\[
B_s = \frac{D_s^m \kappa_s l}{}
\]

Equation 4

The solution diffusion model, as described above, predicts the transport of water as a function of the properties of water, the membrane and the pressure difference applied to the membrane. It is also assumed that the transport of salt is independent of pressure and is driven by the concentration gradient across the membrane. Hence, the rejection of the membrane is related the concentration of solute in the permeate to the concentration in the feed via Equation 5.

\[
R = 1 - \frac{c_{s,p}}{c_{s,x=0}}
\]

Equation 5

2.2. Solution diffusion model combined with thin film theory
As described above, the solution diffusion model relates the permeation of water and salt through the membrane to the concentration at the membrane surface. Since RO membranes provide preferential passage to water over salt, an accumulation of solute molecules at the surface of the membrane on the feed leads to concentration polarisation [6]. Thin film theory has been commonly used to describe mass transfer at the membrane feed side.

![Error! Reference source not found.](b)

Figure 1 shows a schematic diagram of the thin-film theory. The model assumes the presence of a fully developed boundary layer of thickness \( \delta \) on the feed side of the membrane. Additionally, the parallel feed flow to the membrane surface means that the motion of molecules towards the membrane surface is driven by convective flow, within the boundary layer. The rejected solute is assumed to diffuse away from the membrane surface towards the edge of the boundary layer, where the concentration of solute is the bulk concentration \( (c_{s,b}) \). Because the mass transfer is assumed to be limiting only on the feed side of the membrane, the concentration of solute on the membrane wall is considered equal to the bulk concentration of solute in the permeate \( c_{s,p} \). This is justified by the high rejection of RO membranes, which leads to a low concentration of solute in the permeate. [12-15]

A mass balance on the solute leads to Equation 6:

\[
-D_s \frac{dc_s}{dy} + J_w c_s = J_w c_{s,x=l}
\]

Equation 6
Or \[ J_w(c_s - c_{s,p}) = D_s \frac{dc_s}{dy} \] \hspace{1cm} \text{Equation 7}

Integrating Equation 7 using the boundary conditions \( c_s = c_{s,b} \) at \( y = 0 \) and \( c_s = c_{s,x=0} \) at \( y = \delta \) gives a relationship, Equation 8, between the concentration of the solute in the bulk feed solution and its concentration at the membrane surface. The solution requires some knowledge of the mass transfer coefficient of the system, \( k_{a,s} = \frac{D_s}{\delta} \) \cite{12, 15}. This provides a method to estimate the solute concentration immediately at the membrane surface (\( c_{s,x=0} \)) which can be used to account for the impact of concentration polarisation on the observed permeation rates through the membranes.

\[
\frac{c_{s,x=0} - c_{s,p}}{c_{s,b} - c_{s,p}} = e^{J_w k_{a,s}}
\]

\hspace{1cm} \text{Equation 8}

3. Materials and methods

3.1. Materials

Commercial RO membranes (Dow Filmtech SW30-HR and SW30-XLE, Toray Membrane TM 82V, and GE Osmonics AG) were purchased from Sterlitech Corporation, USA. The membranes were stored in a dark and dry location at room temperature. The membranes used in this work and available product information are listed in Table 1. Ultrapure DI water (18.2 MΩ.cm) was obtained from a Centra® R200 purification system (ELGA LabWater, UK). Benzoic acid, ReagentPlus® 99%, Sodium Chloride ReagentPlus® ≥99%, Trimesoyl chloride (TMC) 98% and m-phenylenediamine (MPD) flakes 99% were purchased from Sigma Aldrich, UK. MPD was purified under vacuum sublimation (~1 x 10^{-2} mbar) at (75-80°C) and used fresh each time. Ethanol absolute ≥99.8% AnalaR NORMAPUR®, ACS analytical reagent, N-Hexane ≥99%, AnalaR NORMAPUR® analytical reagent and N-Methyl-2-pyrrolidone (NMP) were purchased from VWR, UK. Polysulfone (Udel® PSU P-3500 LCD MB8) was kindly provided by Solvay Specialty Polymers GmbH, Germany, in the form of beads. Novatexx 2471 polypropylene/polyethylene nonwoven support fabric was purchased from Freudenberg Filtration Technologies Ltd, UK.

3.2. Membrane preparation

3.2.1. Polysulfone (PSF) ultrafiltration (UF) membranes

Polysulfone dope solution was prepared by dissolving the required mass of the polymer beads to achieve a concentration of 18 wt.% and stirred overnight to dissolve at room temperature. The dope solution was allowed to degas for a few hours to remove air bubbles. Polysulfone ultrafiltration membrane was prepared via phase inversion using a continuous casting machine (Speratek, Republic of Korea). The dope solution was poured into a reservoir connected to the casting knife, which was set to 150 µm from the surface of the nonwoven. A film of the dope solution was cast by moving the nonwoven underneath the knife at ~3.8 m.min^{-1}. The polymer film and the nonwoven are then collected on an unwind roll after travelling through a DI water bath kept at 20-24°C. The polysulfone membranes were stored in a DI water bath at 4°C and used within 96 hours of casting to minimise aging.

3.2.2. Polyamide thin film composite (TFC) membranes

Polysulfone UF membranes were used as support for a polyamide layer fabricated by interfacial polymerisation of MPD (2 wt.%) dissolved in water and TMC (0.1 wt.%) dissolved in n-hexane for two minutes. To fabricate the TFC membrane, a piece of the PSF membrane was fitted in a funnel connected to a vacuum pump. A small volume of DI water was filtered through the support followed
by the aqueous phase to impregnate the pores with MPD. The support was then air dried to remove residual droplets on the surface of PSF, and the TMC solution was poured on the membrane. Finally, the excess TMC solution was removed and the reaction was quenched by pouring fresh hexane to dilute the remaining TMC on the membrane surface. In this work, the fabricated membranes are referred to as “analogue” membranes.

3.3. Membrane characterisation

3.3.1. Total organic carbon (TOC) measurement
The TOC due to preservative agents in commercial membranes was characterised using a Sievers InnovOx ES Laboratory TOC Analyzer (Sievers Instruments, UK). A 50 cm x 10 cm piece was cut from each commercial membrane and was dipped in 250 ml of ultrapure DI water. The vials were kept in a cold room at 4°C for 24 hours before performing the measurement along with a blank ultrapure DI water vial for comparison.

3.3.2. Atomic force microscopy (AFM) study
A Multimode 8 (Bruker, CA, USA) atomic force microscope (AFM) equipped with E-type piezo scanner was used to measure the surface roughness of the membranes. Samples were attached onto a magnetic sample disk using double sided adhesive tape. The images were captured under peak force tapping mode using a silicon tip on a nitride lever (MSNL-10, Bruker, CA, USA).

3.3.3. Streaming potential measurement
The streaming potential of the membrane surface was measured using SurPass surface analyser (Anton Paar Ltd., UK). The membranes were dipped in DI water and stored in a cold room at 4°C for 24 hours before the measurement was made. Two 10 mm x 10 mm pieces were cut and fixed to the sample holders using double sided tape. A 1mM KCl solution is then circulated through the system whilst gradually titrating small volumes of 5mM hydrochloric acid or sodium hydroxide in order to control the pH of the system.

3.3.4. X-ray photoelectron spectroscopy (XPS) study
In order to prepare the membrane samples for XPS, the membranes were dipped in DI water for 24 hours and stored in a cold room at 4°C. The membranes were then dipped in ethanol for 10 minutes and left to dry under vacuum (1x10^{-2} mbar) and 30°C overnight. The vacuum was released immediately before scanning the samples to minimise contamination.

The survey spectra and core level XPS spectra were recorded from at least three different spots of size 400 µm on the sample surface. Samples were introduced into the instrument via a turbo molecular pumped entry lock. The entry lock was pumped for about 15 minutes before the sample was introduced into the analysis chamber. Monochromatic Al K-Alpha (1486.68 eV) X-ray excitation was used to study XPS scans using an ion pumped VG Microtech CLAM 4 MCD analyser system. The analyser was operated at constant pass energy of 200 eV for wide scans and 20 eV for narrow scans. An electron flood gun was used to overcome any sample charging under photoelectron emission.

3.3.5. Attenuated total reflection – Fourier transform infrared spectroscopy (ATR-FTIR) study
FTIR spectroscopy of the membranes in the ATR mode was acquired using a Spectrum 100 FTIR Spectrometer (PerkinElmer, UK). The membranes were dipped in ultrapure DI water for 48 hours and then dried under vacuum (1x10^{-2} mbar) overnight, and the spectra were acquired immediately after releasing the vacuum to minimise the broad OH stretch around 3600-3300 cm^{-1} [16] caused by water adsorption on the membrane surface. Background correction was applied to the spectra; and the absorbance is normalised relative to the maximum value of absorbance recorded in each spectrum.
3.3.6. UV-vis absorbance measurement
The UV-vis transmittance of benzoic acid solutions was measured using a UV-1800 UV-VIS spectrophotometer (Shimadzu Ltd., UK) via transmission mode using quartz cuvettes. The spectrophotometer was used to measure the absorbance at 228 nm and 273 nm to determine the concentration of benzoic acid in solution.

3.4. Membrane Performance measurement

3.4.1. Crossflow filtration tests
The performance of the membranes in SWRO was tested in a custom built continuous crossflow rig. The process flow diagram of the rig is shown in Error! Reference source not found. in the supplementary information. The rig consisted of 12 custom built stainless steel crossflow cells, with an active membrane area of 0.00138 m$^2$ per cell. The cells were arranged in three parallel lines, each line containing four cells in series. The rig was equipped with multiple flowmeters and pressure gauges, in order to closely monitor and control the testing parameters. A PID temperature controller was used to keep the temperature of the water in the feed tank, approximately 5 L, at constant temperature of 30.0 ± 0.5°C.

After loading a membrane coupon in each cell, DI water was circulated through the system at a low flowrate to avoid damaging the membranes with sudden change in pressure. The low flowrate was maintained for approximately 10 minutes to allow all the air trapped in the tubing to escape. The flowrate and pressure were gradually increased to 50 L.h$^{-1}$ and 60 bar, respectively. A sample of water was collected to determine the initial flux of the membranes. The membranes were held at these conditions until a steady state was reached, which typically required 72 hours. Several samples were taken to ensure the permeance reached the steady state. Sodium chloride was then added gradually to reach the required bulk concentration, from 0 to 70 g.L$^{-1}$, to emulate the feed conditions in water desalination, including in high recovery brackish water and seawater desalination. After adding sodium chloride, the system was allowed to reach equilibrium before taking a sample. In order to avoid corrosion caused by prolonged exposure to sodium chloride solutions, the system was washed with DI water once a day during each run; a run typically lasted 10-14 days.

The performance of the membranes was tested by collecting permeate samples from each cell for 10 – 30 minutes, during which 20 - 50 ml were typically collected. The sampling duration was extended to minimise human error introduced in time measurement. The exact volume of water collected was determined by weighing the sample vials before and after sampling using a mass balance, with accuracy off ± 0.01 g. The flowrate of permeate was converted to flux using Equation 9, and the salt flux was calculated using Equation 10. The concentration of sodium chloride in the feed and permeate was determined by measuring the solution conductivity using an HI-8733 multirange conductivity meter (HannaInstruments, UK). The conductivity meter was periodically calibrated with multiple standard solutions, as well as several sodium chloride solutions, to ensure accuracy in determining the concentration of sodium chloride.

$$F_p = A \times J_w$$  \hspace{1cm} \text{Equation 9}

$$J_s = J_w \times c_{s,p}$$  \hspace{1cm} \text{Equation 10}
3.4.2. Estimation of the mass transfer coefficient

The mass transfer coefficient in the crossflow cells was estimated using the dissolution of benzoic acid, which is sparingly soluble in water. This technique was previously applied in a similar system [17]. A diagram of the system used for this measurement is shown in Figure 2a.

In short, a plastic replica of the cells was made with a 2 mm deep hole, diameter of 35 mm, which was drilled where the membrane would typically reside. A disc of benzoic acid was formed within this opening by melting benzoic acid powder (melting point of 122°C), and allowing it to cool and crystallise. Thus providing a disc of benzoic acid where the membrane would usually be. The rate of dissolution of benzoic acid was evaluated by circulating DI water from a feed tank, at 30°C, through the cell at different flowrates and regularly taking samples of the bulk solution from the feed tank. The concentration of benzoic acid was measured by UV-vis absorption at 228 nm and 273 nm. The spectra were compared to a 20-point calibration curve of benzoic acid solutions Error! Reference source not found., to determine the concentration of benzoic acid in the solution.

The mass transfer coefficient $k_{a,BA}$ in the cells could then be calculated using Equation 11, where $c_{BA}^*$ is the saturation concentration of benzoic acid at 30°C. The volume of liquid in the system was assumed to be constant; only five 1 ml samples were taken in each experiment. The effect of pressure on the mass transfer coefficient was assumed to be negligible, and the experiments were performed at 5-10 bar, to avoid damaging the plastic cells.

The surface of the benzoic acid disc was assumed to be sufficiently smooth to not influence the rate of dissolution. The smooth surface was achieved by heating and cooling the disc multiple times; the surface was manually polished using sand paper down to grit size of P2000, with every cooling step. This allowed using direct force on the disc, which revealed the location of defects in its structure. Additional benzoic acid was added and the melting process was restarted until a defect-free and smooth surface was achieved.

\[
\ln \frac{c_{BA}^*}{c_{BA}^* - c_{BA}} = \frac{k_{a,BA} \times A \times t}{V}
\]

Equation 11

Once the value of mass transfer coefficient of benzoic acid in the system was obtained, the value of mass transfer coefficient of sodium chloride, $k_{a,s}$, was estimated using a correlation of the form presented in Equation 12. This links the properties of the solution, operating parameters and some geometry-dependant parameters (specific to the system) to the mass transfer coefficient. The exponents $x_1$-$x_4$ can be obtained empirically and are available in literature for some geometries [6, 17]. Because the cells used were identical in channel height and length, Equation 12 could be reduced to Equation 13. The value of $k_{a,BA}$ obtained from the dissolution of benzoic acid using Equation 11 was used to estimate the value of the mass transfer coefficient of sodium chloride $k_{a,s}$.

\[
Sh = x_1 \cdot Re^{x_2} \cdot Sc^{x_3} \left( \frac{h}{L} \right)^{x_4}
\]

Equation 12

\[
\frac{k_{a,s}}{k_{a,BA}} = \left( \frac{\eta_s}{\eta_{BA}} \right)^{x_3-x_2} \left( \frac{D_s}{D_{BA}} \right)^{1-x_3}
\]

Equation 13
4. Results and discussion

4.1. Estimation of the mass transfer coefficient

Figure 2b and Figure 2c show the benzoic acid disc before and after performing the experiment. The dissolution of the acid appeared to be uneven across the disc, indicating spatial variation in the mass transfer coefficients. Since the concentration of benzoic acid was monitored in the bulk of the feed tank, the calculated mass transfer coefficient is representative of the space averaged (overall) transfer coefficient over the area of the disc.

The value of the mass transfer coefficient was calculated from Equation 11 using the data shown in Error! Reference source not found.. The value of the diffusivity of benzoic acid, $D_{BA}$, was taken to be $0.8 \times 10^{-9}$ m$^2$.s$^{-1}$ [17]. The solubility limit of benzoic acid in water was obtained by interpolation of the data reported in [18] (pg. 134). A systematic increase in the value of $k_{a,BA}$ was observed from 50 – 150 L.h$^{-1}$ as expected, Figure 2d. The mass transfer coefficient of sodium chloride, $k_{a,s}$, was estimated using Equation 13 and the results are shown in Figure 2e. A small decrease in the estimated value of the mass transfer coefficient with increasing concentration of sodium chloride due to the effect of sodium chloride on the volumetric properties of the solution [19, 20], and the diffusivity of sodium chloride [21].

![Figure 2](image-url)

**Figure 2.** (a) Process flow diagram of the setup used to conduct the dissolution experiments. Picture of the lower section of the plastic cell used with the embedded benzoic acid disc (b) before (c) after performing the experiment. (c) Mass transfer coefficient calculated from the rate of...
dissolution of benzoic acid. (d) Calculated mass transfer coefficient of sodium chloride as a function of the solution concentration at different crossflow velocities.

The constants \( x_1 \) to \( x_4 \) required to estimate the mass transfer coefficient were taken from [6] for a radial cross flow system, although the values used in [17] yielded similar results. The estimated value of \( k_{as} \) was around \( 1 \times 10^{-4} \text{ m.s}^{-1} \) at 50 L.h\(^{-1}\); and the results are shown in Figure 2e. The validity of the estimated value of mass transfer coefficient is discussed in the supplementary information.

4.2. Membrane characterisation

Table 1 contains a list of the commercial membranes used in this work. These membranes are made using different chemistries and are intended for different applications. TOC analysis confirmed that all the membranes had water soluble preservatives or coatings compared to the control sample of DI water, Error! Reference source not found..

Table 1. Product information of commercial membranes used in this study as reported by Sterlitech Corporation (www.sterlitech.com).

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Manufacturer</th>
<th>Chemistry</th>
<th>Feed Water</th>
<th>Permeate flux and rejection</th>
<th>Testing Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>SW30-HR</td>
<td>Dow Filmtec</td>
<td>Polyamide-TFC</td>
<td>Seawater</td>
<td>25.4 L.m(^{-2}).h(^{-1}) 99.82%</td>
<td>32,000 ppm NaCl, 55 bar(^{(a)})</td>
</tr>
<tr>
<td>SW30-XLE</td>
<td>Dow Filmtec</td>
<td>Polyamide-TFC</td>
<td>Seawater</td>
<td>38 L.m(^{-2}).h(^{-1}) 99.8% (^{(a)})</td>
<td>32,000 ppm NaCl, 55 bar(^{(a)})</td>
</tr>
<tr>
<td>X-201</td>
<td>Trisep</td>
<td>Polyamide-urea-TFC</td>
<td>Industrial / Wastewater</td>
<td>43.4 L.m(^{-2}).h(^{-1}) 99.0-99.5% (^{(a)})</td>
<td>2,000 ppm NaCl, 15.5 bar (^{(a)})</td>
</tr>
<tr>
<td>TM 82V</td>
<td>Toray Membrane</td>
<td>Polyamide-TFC</td>
<td>Seawater</td>
<td>45.8 L.m(^{-2}).h(^{-1}) 99.7%</td>
<td>-</td>
</tr>
<tr>
<td>AG</td>
<td>GE Osmonics</td>
<td>Polyamide-TFC</td>
<td>Brackish</td>
<td>43.8 L.m(^{-2}).h(^{-1}) 99.0-99.5% (^{(a)})</td>
<td>2,000 ppm NaCl, 15.5 bars (^{(a)})</td>
</tr>
</tbody>
</table>

\(^{(a)}\) Data taken from the manufacturer’s website / membrane specification sheet
AFM, zeta potential measurements were investigated to probe the surface properties of the membranes. The AFM images are shown in Figure 3. All the membranes, including the Analogue membrane, showed the crumpled structure commonly found in RO membranes [22, 23]. The membranes showed comparable RMS roughness, Table 2. The seawater treatment membranes, SW30-XLE and TM 82V, had a RMS roughness of 78 nm, similar to the analogue membrane. On the other hand, the membranes intended for treatment of waste and brackish water, X-201 and AG, showed RMS surface roughness below 60 nm.

### Table 2. RMS roughness of RO membranes at 5 µm x 5 µm.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>RMS roughness [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analogue</td>
<td>78.5 ± 9.3</td>
</tr>
<tr>
<td>SW30-HR</td>
<td>54.1 ± 18.9</td>
</tr>
<tr>
<td>SW30-XLE</td>
<td>78.0 ± 18.2</td>
</tr>
<tr>
<td>X-201</td>
<td>57.8 ± 7.2</td>
</tr>
<tr>
<td>TM 82V</td>
<td>78.6 ± 13.6</td>
</tr>
<tr>
<td>AG</td>
<td>48.0 ± 4.6</td>
</tr>
</tbody>
</table>

The charge on the membrane surface was characterised using zeta potential measurement; and the results are shown in Figure 4. All membranes had a negative surface charge around pH of 7, which is expected in RO membranes formed by interfacial polymerisation [3, 24, 25]. At a pH of 7, the range of zeta potential measurement of the membranes was between -20 and -50 mV. The analogue, X-201 and TM 82V membranes were strongly negatively charged, around -50mV. The membranes with the weakest negatively charged surface were the SW30-HR and the SW30-XLE, which are used in seawater desalination. This is because the surface charge is more significant at lower salt concentrations (<3 g.L⁻¹), due to the effect of Donnan potential on the rejection of ions. At higher salt concentrations, the effect of Donnan potential is weakened and its effect on the rejection diminishes. [3]
Figure 4. Zeta potential of the surface of thin film composite RO membranes.

XPS analysis was used to characterize the chemistry of the thin film composite membrane surface. Due to the low penetration depth of the photon beam [26], this study provides information regarding the chemical environment localised at the top surface of the separating layer. The results of the survey scans are presented in Figure 5. The carbon content of the analogue membrane was 74.9 at.% with equal nitrogen and oxygen content, similar to the expected value of a fully crosslinked polyamide network [27]. The commercial membranes investigated in this work showed significant deviation from the atomic structure predicted for a fully crosslinked polyamide network formed by the interfacial polymerisation of MPD and TMC. Apart from the X-201 membrane, the commercial membranes had a higher oxygen content than nitrogen. It is noteworthy that the atomic structures of the SW30-HR and SW30-XLE membranes were similar to the predicted structure for a fully linear polyamide network via the polymerisation reaction of MPD and TMC [27]. Nevertheless, the variations in the chemical structures of the membrane surface could be the result of additional coating layers added by the manufacturers for various functions, such as improving the fouling resistance of the membranes [26]. This is also supported by the results of the C1s narrow scans of the SW30-HR and the SW30-XLE membranes, Error! Reference source not found.b and Error! Reference source not found.c, which show different chemical environments of carbon compared to that of the fully crosslinked polyamide network formed by the interfacial polymerisation of MPD and TMC of the analogue membrane, shown in Error! Reference source not found.a.
Furthermore, combining the results of the XPS spectra with the results of ATR-FTIR, which has a deeper sampling field, could be used to develop a better understanding of the chemical properties of the membranes. The FTIR and C1s deconvoluted XPS spectra have been included in the supplementary information, Error! Reference source not found. and Error! Reference source not found., respectively. A few assigned peaks in the FTIR spectra are presented in Error! Reference source not found. and Error! Reference source not found..

4.3. Membrane performance

The transport properties of the membranes measured at constant $\Delta P = 60$ bar and temperature $T = 30^\circ C$ are presented in Figure 6. The reduction in observed rejection, shown in Figure 6a, agrees with the predictions of the solution diffusion model [6, 11]. This is explained by the increase in permeate salt concentration $c_{s,p}$ as the concentration of salt in the feed solution was increased, in addition to the simultaneous reduction in water flux (applied pressure remains constant while osmotic pressure increased) and increase in the concentration of salt on the membrane wall, Equation 3. Figure 6b shows the rejection of RO membranes with the estimated concentration at the membrane surface ($c_{s,x=0}$) after applying the mass transfer coefficient corrections to experimental data presented in Figure 6a. A detailed discussion on the significance of errors on the results is presented in the supplementary information. By comparing Figure 6a and Figure 6b, the rejection of the membranes increased when using the concentration ($c_{s,x=0}$), at high salt concentrations, indicating some mass transfer limitations. This shows that concentration polarisation may impact the observed performance of RO membranes even under mildly concentrated conditions. Therefore, it is necessary to use the solution diffusion model and film theory to calculate the permeance and rejection of RO membranes when using non-dilute conditions.
The observed permeance of the membranes, Figure 6c, showed decreasing permeance as the concentration of sodium chloride in the bulk solution was increased. The filtration experiments were performed at constant applied pressure $\Delta P$ (60 bar) and temperature (30°C). This trend is expected due to the discrepancy between the osmotic pressure at the membrane surface compared to the osmotic pressure of the bulk solution, which is expected to be more severe at higher salt concentrations.

Assuming the membranes had a constant water permeance, and considering the exponential term $e^{Jw K ax}$ in Equation 8, we expected to find a greater reduction in the observed permeance as the water
flux for the membranes with greater water flux. In other words, the impact of concentration polarisation is expected to increase as the stage cut increases, for a constant feed flowrate. However, the observed permeance decreased by 46% for the membrane with the largest water flux, X-201, while the observed permeance of the SW30-XLE membrane saw the largest reduction at 57%. Moreover, the observed permeance of the Analogue membrane decreased by 10% only. This indicates the water permeance of the membranes may not be constant for all concentrations of sodium chloride. This was confirmed by applying the mass transfer corrections, Figure 6d, where the permeance of RO membranes was dependent on salt concentration at the higher end of the experimental conditions. Comparing the calculated permeance of RO membranes with and without applying mass transfer corrections, Figure 6c and Figure 6d respectively, also indicate the presence of mass transfer limitations in the systems, which can be accounted for by using the solution diffusion model combined with film theory.

Figure 7 shows the permeance of salt and water through the investigated RO membranes as a function of the driving force, as predicted by the solution diffusion model. As the concentration of salt at the membrane surface increased, leading to higher concentration driving gradient across the membranes, the salt permeance through the membranes, shown in Figure 7a, decreased for the TM 82V (by 55%), X-201 (by 48%) and SW30-XLE (by 38%) membranes. The salt permeance of the analogue membrane remained constant throughout the testing range, whilst the salt permeance of the SW30-HR and AG membranes fluctuated significantly during testing; and showed neither increasing nor decreasing trends.

The permeance in the solution diffusion model is a function of diffusion coefficient of component $i$ ($D_i^m$), the partitioning coefficient ($\kappa_i$) and the membrane thickness ($l$). Where component $i$ denotes water or salt, as shown in Equation 2 and Equation 4. It is important to note that the solution diffusion model does not require these parameters to be constant [11]. Therefore, the observed changes in salt and water permeance as a function of salt concentration can be explained in light of
the solution diffusion model by variations in the diffusivity and partitioning coefficients, or even variations in the thickness of the separating layer of the membranes.

The change in salt permeance, Figure 7a, could be caused by the effect of sodium chloride on the chemical potential of water, which influences the degree of polymer swelling and relaxation, and the time frame of these processes [4]. Moreover, the swelling of the membranes has also been reported to change their thickness, which would also impact the apparent permeation of both water and sodium chloride [28]. These changes were found to be reversible, shown in Error! Reference source not found. in the supplementary information. This is expected since swelling is a physical process; and the changes in the chemical potential of the feed solution are not sufficient to overcome the energy barrier required to cause permanent modification to the highly crosslinked polyamide network of the RO membranes.

Similarly, the diffusion and partitioning coefficients of water would be expected to change as the concentration of sodium chloride was varied. Figure 7b shows the effect of varying the driving force \( \Delta P - \Delta \Pi_{x=0} \) on the water permeance of the RO membranes. The results show that for all the membranes tested, the permeance was independent of salt concentration at the membrane surface below 45 g.L\(^{-1}\). This is in agreement with studies conducted up to 20 g.L\(^{-1}\) [7]. When the concentration at the membrane surface exceeded 45 g.L\(^{-1}\), the membranes tested showed three different trends. The permeance of the SW30-HR, SW30-XLE and TM 82V membranes decreased by approximately 50%. The water permeance of the X-201 and AG membranes did not change significantly, whilst the permeance of the analogue membrane doubled as the concentration of sodium chloride increased.

Predicting the behaviour of RO membranes in different environments remains challenging. Foglia et. al. showed that even for films made by the interfacial polymerisation of MPD and TMC, changing the reaction conditions yielded films with varying degrees of water uptake and swelling [29]. The observed changes in the transport of water and salt through the membranes are not correlated to the examined physicochemical properties of the membrane surface. The evidence also suggests that the change in diffusivity and partitioning coefficient of sodium chloride is independent of those of water. This is because the reduction in salt permeance was observed throughout the testing conditions, whilst the changes in water permeance were only observed at high salt concentrations. Moreover, the water permeance of the analogue membrane increased, while the salt permeance remained constant as c\(_s,b\) was increased. The X-201, however, displayed the opposite trend with the water permeance remaining constant, while the salt permeance through the membrane decreased.

5. Conclusions
In this work, the influence of changing the concentration of sodium chloride in the feed solution on the transport of water and salt through different RO membranes, as well as a thin film composite membrane fabricated by the interfacial polymerisation of m-phenylenediamine (MPD) and trimesoyl chloride, was examined. The membranes were tested at 60 bar applied pressure and feed concentration up to 70 g.L\(^{-1}\), and the permeance was calculated from membrane flux using the solution diffusion model combined with thin film theory. This enabled in-depth analysis of the transport of water and salt through a range of RO membranes.

The results showed that the salt permeance across the membranes behaved consistently throughout the testing range. A linear reduction in salt permeance was observed in some of the RO membranes, and the salt permeance remained constant for other membranes, including the Analogue membrane. All the tested membranes maintained constant water permeance below 45 g.L\(^{-1}\).
However, when the salt concentration on the membrane surface exceeded 45 g.L\(^{-1}\), the water permeance through the membranes either increased, remained constant or decreased. We have shown that the changes in salt permeance and water permeance were not correlated. We have also demonstrated the independence of the variation in water permeance and salt permeance from the surface properties of the membranes. Finally, we attributed these changes in the transport properties of the membranes to the effect of salt concentration on the degree and time-frame of membrane swelling and deswelling, which is manifested as variations in the diffusivity and partitioning coefficients of water and salt into the membranes, as well as the membrane thickness.

The membranes used in this study represent some of the most commonly used commercial membranes in desalination, as well as MPD-TMC polyamide TFC membranes, the most commonly investigated chemical reaction for the fabrication of RO membranes. The data reported here may provide insight for improved transport models for RO membranes in future studies, as well as open a window for more accurate process models investigating the optimisation of the design and operation of SWRO systems.

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7. Nomenclature
A – Active area [m\(^2\)]
a - Activity
B – Permeance [m\(^3\).m\(^{-2}\).s\(^{-1}\).Pa\(^{-1}\)] converted to [L.m\(^{-2}\).h.bar\(^{-1}\)]
c – Concentration [mol.m\(^{-3}\)] converted to [g.L\(^{-1}\)]
c\(^*\) - saturation concentration [mol.m\(^{-3}\)] converted to [g.L\(^{-1}\)]
D – Diffusion coefficient [m\(^2\).s\(^{-1}\)]
F – Flowrate [L.h\(^{-1}\)]
h – Feed channel height [m]
J – Flux [m\(^3\).m\(^{-2}\).s\(^{-1}\)] converted to [L.m\(^{-2}\).h\(^{-1}\)]
k\(_a\) – Mass transfer coefficient [m.s\(^{-1}\)]
\(\ell\) – Thickness of the separation layer of the membrane [m]
L – Feed channel length [m]
m – Molal concentration [mol.kg\(^{-1}\)]
P – Pressure [bar]
R – Rejection
Re – Reynolds number
R\(_g\) – Universal gas constant [8.314 J.mol\(^{-1}\).K\(^{-1}\)]
R\(_o\) – Observed rejection
Sc – Schmidt number
Sh – Sherwood number
T – Temperature [K]
t – Time [s]
V – volume [m\(^3\)]
x\(_1\), 2, …. - Constants
z - Mole fraction

Greek alphabet
\(\gamma\) – Activity coefficient
\(\nu\) – Molar volume [m\(^3\).mol\(^{-1}\)]
η – Kinematic viscosity [Pa.s]
Π – Osmotic Pressure [Pa]
φ – Osmotic coefficient
δ – Boundary layer thickness [m]

Subscripts
b – Bulk
BA – Benzoic acid
f – Feed
i – Species which could be either solvent or solute
p – Permeate
r – Retentate
s – Solute (sodium chloride)
w - Water
x – Point with coordinate x in a membrane of thickness l
y – Point with coordinate y in a boundary layer of thickness δ

Superscripts
m – Membrane phase

8. References