Characterization and Membrane Stability Study for the

Switchable Polarity Solvent *N,N*-

Dimethylcyclohexylamine as a Draw Solute in Forward

Osmosis

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Abstract

Commercially available reverse osmosis and forward osmosis thin-film composite membranes were assessed for long-term chemical stability when immersed in 10 molal *N,N*-dimethylcyclohexylammonium hydrogen carbonate draw solution, a model switchable polarity solvent draw solute for forward osmosis. Membrane performance was monitored with reverse osmosis testing, including rejection of 2000 ppm sodium chloride (NaCl), for three commercial reverse osmosis membranes—Dow BW30, SW30HR, and SW30HR with polyester backing layer removed—and a commercial forward osmosis membrane (HTI TFC). The RO membranes were observed to be mostly unaffected by exposures up to 90 days while the HTI TFC suffered a sharp increase in both water permeance and sodium chloride permeability, manifesting itself as a reduction in intrinsic rejection of NaCl from 95% to 82%. The as-received HTI TFC membrane was characterized for osmotic water flux, where it was found the water flux was very insensitive to draw solute concentration in both the pressure-retarded osmosis and forward osmosis operating modes. Reverse permeation of the draw solute was highly variable, despite lower variability in the forward water flux. Forward osmosis desalination of a 0.5 molal sodium chloride feed with the HTI TFC membrane and 10 molal draw solution indicated higher rejection (ca. 98.7) than under reverse osmosis testing, albeit with lower flux and the presence of reverse permeation of the draw solute. The overall results imply that a forward

osmosis membrane with acceptable tolerance to switchable polarity solvent draw solutions can be developed within the existing framework of polyamide-on-polysulfone membrane chemistry.

1. Introduction

Forward osmosis (FO) is an emergent technology that has been investigated as a method for both low-cost desalination and the dewatering of industrial water streams such as concentrated brines and produced water. One of the unique strengths of FO is the ability to generate driving force using any number of draw solutes. Numerous draw solutions have been proposed for FO, but the most extensively utilized draw solute, especially in research environments, is sodium chloride. Other commonly utilized draw solutions have included magnesium and ammonium salts[1,2]. These solutes are generally cheap and easy to work with, and thus it is easy to probe membrane performance. When considering the FO process as a whole, though, draw solute recovery is often overlooked. Some technology platforms consider the use of RO to concentrate the draw solute, but the cycle of FO followed by a mechanical osmotic separation (e.g. RO, NF, UF) is energetically unfavorable to concentrate the draw solution[3]. Such approaches do offer “dual barrier” or reduced fouling benefits to certain separations, but they may not offer substantial cost savings. Thermolytic solutes, such as the ammonia-carbon dioxide draw solution, commercialized by Oasys Water (Boston, MA) and extensively studied [2,4–6] by the authors are considered as alternatives. Rather than use mechanical force, the ammonia-carbon dioxide draw solution utilizes low-grade heat to drive the decomposition of ammonium bicarbonate into sparingly soluble carbon dioxide and readily-distillable ammonia. However, as ammonia is a small molecule (17 Da) and excess free ammonia is present in the draw solution, ammonia can permeate into the feed solution, necessitating treatment of the concentrated feed[5]. Additionally, polyamide thin-film composite (TFC) membranes have been shown to allow rapid exchange of feed cations (sodium) and ammonia

across the membrane via ion-exchange phenomena[7,8]. Alternative volatile and nonvolatile amines have been proposed as draw solutes in FO[9,10] and in particular, trimethylamine (59.11 Da) has been shown not to exhibit the same ion-exchange phenomena, which has been attributed to its large size[11].

The switchable polarity solvent (SPS) FO process utilizes aliphatic tertiary amines which have limited miscibility in water in their neutral, unprotonated, state[12]; we restrict usage of the term “SPS” only to switchable solutes having this particular switching behavior. When protonated via reaction with an acid, such as carbonic acid, these amines form stable ammonium salt complexes. The amine salts are stable and water soluble. In the case of amine bicarbonate salts, the aqueous salt can be decomposed to the parent amine and acid via thermal decomposition of the salt or by stripping CO₂ out of the solution with an inert gas. The deprotonated amine is no longer water soluble and phase separates. A wide range of SPS materials have been characterized[13], however *N,N*-dimethylcyclohexylamine (DMCHA) and its corresponding ammonium bicarbonate salt, *N,N*-dimethylcyclohexylammonium hydrogen carbonate (DMCHAH-HCO₃) has commonly been used as a SPS material for a variety of applications due to its low toxicity, relative inexpensiveness and availability, and ease of forward switching[14–16]. DMCHA has a solubility in DI water of approximately 18 g/L (~1.8% by mass), but in its switched form, the DMCHAH-HCO₃ complex has a solubility of ~77% (~51.8% by DMCHA)[13]. The chemical structure and switching cycle for DMCHA is shown schematically in **Figure 1**. The solubility of DMCHA, and similar amines, in water over a wide range of temperatures is limited[17], and this ensures good separation if the switching agent, CO₂, can be adequately stripped by heat and/or gas. The comparatively large size of DMCHA (127.23 Da), and related SPS materials, correlate to low permeability in polyamide membranes,

as compared to smaller nitrogen compounds including ammonia and trimethylamine. A previous study with DMCHA measured the RO rejection of a saturated solution of DMCHA in water (18 g/L) at 99.7%[18], and characterization of RO membranes with molecules of similar size ranges indicate that rejections of 60-100% can be expected[19], in part by modulating the crosslink density of the polyamide selective layer.

Figure 1: Chemical cycle of the “forward” and “reverse” switching process for *N,N*-dimethylcyclohexylamine to *N,N*-dimethylcyclohexylammonium hydrogen carbonate.

DMCHA, as a solvent, is relatively aggressive at plasticizing some plastics or extracting plasticizers from others. Objects made of polyethylene or polypropylene were observed to become flexible and deform under light but continuous load, e.g. a polypropylene centrifuge tube lying on its side. Many materials, such as flexible plastic tubing, containing plasticizers become brittle or simply disintegrate after exposure to DMCHA, but DMCHA does not appear to form solutions with most polymers. On the other hand, DMCHA is one of the most affordable SPS materials, as it is commercially utilized as a gel catalyst in the production of urethanes and is widely available. Thus given its high aggressiveness and low cost DMCHA is the best candidate SPS material for which to test membrane compatibility. Subsequent “generation 2” SPS

materials, such as 1-cyclohexylpiperidine (CHP), are less chemically aggressive and the DMCHA should serve as a form of accelerated aging study. Characterization of the recovery of SPS materials[20] have shown that CHP reverts to its non-polar form more readily than DMCHA when deswitching via heating. Despite the disadvantages of DMCHA, preliminary simulations of the energy requirements of a DMCHA-based FO desalination system indicate that such a system could operate with favorable “equivalent” energy consumption compared to reverse osmosis desalination or thermal desalination[21].

The objective of this study was to assess the suitability of a commercial TFC FO membrane from Hydration Technologies Innovations, as well as the stability of commercial RO membranes under long-term exposure to the DMCHAH- HCO_3 to determine the feasibility and guide the development of a tailored SPS-FO membrane. Previous studies on the DMCHA demonstrated that cellulose acetate membranes generate flux of water into the SPS solution against a feed of sodium chloride, however due to membrane degradation, only the initial flux is reported and the rejection of sodium chloride as well as the reverse flux of DMCHA into the feed were not determined[18]. It is not immediately certain whether polyamide selective layers will retain DMCHA or similar SPS materials at high concentrations or whether polyamide selective layers will be selective for salt in the presence of DMCHA. To this aim, membranes were immersed in concentrated DMCHAH- HCO_3 draw solution for up to 90 days and their tolerance to the SPS material was assessed by measuring changes in the membranes’ water permeance and sodium chloride permeability in reverse osmosis. Changes in the membrane water permeance and solute permeability could indicate degradation of the membrane selective layer or support layer.

2. Materials and methods

2.1. Membranes and materials

Membranes for this study were provided by Dow Water & Process Solutions (SW30HR and BW30) and a thin-film composite FO membrane by Hydration Technologies Innovations (HTI TFC). *N,N*-dimethylcyclohexylamine (99%) was purchased from both Acros Organics (Geel, Belgium) and Sigma Aldrich (St. Louis, MO). “Bone Dry” carbon dioxide was purchased from Airgas, Inc. (Radnor, PA). Sodium chloride was purchased from Fisher Scientific (Pittsburgh, PA). Deionized water was produced via a Millipore Integral 10 unit (Millipore Corporation, Billerica, MA).

2.2. Switching procedure

To switch the organic DMCHA into the corresponding soluble salt at a concentration of 10 molal, water and DMCHA were mixed in the following quantities of 3817 g of amine (30 moles) are mixed with 3541 g of water are mixed and sparged with CO₂ in an open vessel until a clear homogenous product resulted after 2-3 hours. The mass of the resulting product was compared to the expected mass of 30 moles of DMCHAH-HCO₃ at 10 molal (8677.8 g) and deviation from that value was assumed to be due to removal of water during the sparging of CO₂. The formation of the DMCHA salt is exothermic and the draw solution warmed up to approximately 50 °C.

2.3. Membrane exposure procedure

Membranes were exposed to concentrated DMCHAH-HCO₃ by direct immersion of the relevant membranes in a glass jar at a ratio of 1 liter of 10 molal DMCHAH-HCO₃ to 36 membrane coupons (2168 cm²). After the allotted time period, 6 membrane coupons were removed from each jar and rinsed in three volumes of 500 mL of DI water, then let sit in 500 mL

of DI water for 3 days with a change of water occurring each day. One batch of Dow SW30HR membranes was removed from its polyethylene terephthalate (PET) layer by peeling the membrane structure away from the PET.

2.4. Characterization and stability testing using reverse osmosis

After three days immersion in DI water, membranes were loaded into a 6-cell (2 parallel rows of 3-in-series) RO system and flushed with DI water in closed-loop recirculation until 100 mL of permeate had collected from each cell. The system was then flushed and refilled with DI water for water permeance testing at 225 psi. The system was brought to 2000 ppm of sodium chloride and the water and sodium chloride flux were observed. Sodium chloride rejection was measured using an Oakton 11 series conductivity probe (Oakton Instruments, Vernon Hills, IL).

The external mass transfer coefficient was estimated from an established correlation for the Sherwood number which has been widely employed for forward osmosis[22], shown in **Equation 1**. The viscosity, diffusion coefficient, and density of sodium chloride solution at a range of concentrations were obtained [23,24] and fitted to an interpolating polynomial to determine the appropriate mass transfer coefficient at 2000 ppm (~34 mM). At these concentrations, and for a feed flow rate of 1 liter/minute, the mass transfer coefficient for sodium chloride is estimated to be 67.8 liter/m²·hr (18.8 μm/s).

$$NSh = \frac{NReNScdh}{\epsilon} = kdhD \quad (1)$$

The intrinsic membrane rejection is calculated as

$$\%R_{apparent} = -\frac{c_{permeate}}{c_{membrane}} \quad (2)$$

The intrinsic membrane rejection adjusts the feed concentration for concentration polarization effects that cause the concentration of solute at the membrane surface (“ $c_{membrane}$ ”) to be higher

than in the bulk solution. This removes the impact of system hydrodynamics from the observed membrane rejection. The concentration at the membrane surface can be estimated from film theory using the mass transfer coefficient k defined in Equation 1. The resulting expression for the interfacial concentration of solute is[25]

$$c_{\text{membrane}} = c_{\text{bulk feed}} e^{J/k} + c_{\text{permeate}} - e^{J/k} \quad (3)$$

which can be substituted into Equation 2 to determine the intrinsic rejection.

2.5. Custom-built FO system

To characterize the performance of the DMCHAH-HCO₃ draw solution in FO, it was necessary to construct a “solvent-tolerant” FO system. The system was essentially identical to other systems[26], but was built with sufficiently solvent-tolerant materials. Flexible tubing lines were made of PVC with an interior PFA lining for chemical resistance. Flow rate was measured using a stainless steel oval gear flowmeter (Great Plains Industries, Wichita, KS). The membrane test cell was fabricated in-house from acetal. Draw and feed solutions were stored in high-density polyethylene tanks with bulkhead fittings made of PTFE with PFA-coated silicone o-rings. The o-rings used in the test cell were Viton, but were changed after every test. Black Viton and blue fluorosilicone o-rings were found to be degraded by exposure to the DMCHA, the fluorosilicone disintegrating while the Viton o-rings developed cracks after long-term exposure to DMCHA followed by drying. All additional components were made of various grades of stainless steel (316, 304, 303) or PTFE.

2.6. Forward and pressure-retarded osmosis characterization

The FO and PRO performance of the concentrated DMCHAH-HCO₃ was measured in the solvent tolerant FO system utilizing four liters of DI water and 1.7 kg of 10 mol/kg

DMCHAH-HCO₃ draw. The mass flux out of the feed tank was measured and the concentration of the draw solution was periodically adjusted by adding water to decrease the concentration of the DMCHAH-HCO₃.

Due to the high viscosity of the amine (~15 cP), the pump speed on the draw side was set to the maximum that could be obtained without exceeding 5 psi pressure with the pressure regulating valve full-open, i.e. with minimal restriction to flow. Flow rate decreased as the draw was diluted and the pressure valve was closed to maintain 5 psi pressure. For the concentrations of 10, 7.5, 5, and 2.5 molal DMCHAH-HCO₃, the average flow rates were 0.81, 0.77, 0.67, and 0.583 liter/minute, respectively (17.1, 16.3, 14.1, and 12.3 cm/s, respectively). The dilute feed side was controlled at 1 liter/minute and 5 psi pressure.

The external mass transfer coefficient can be estimated from the Reynolds number, the Schmidt number, and a correlation for the Sherwood number as shown in Equation 1. Utilizing physical property data for the DMCHAH-HCO₃ system[20], the density, diffusivity, and dynamic viscosity at 25 °C were fit to polynomials. This data was assumed to be extendable to 20 °C and can be found in the supporting information. Estimation of the mass transfer coefficients for DMCHAH-HCO₃ shows minor differences between a test operated with a constant flow rate of 1 liter/minute compared to the flow rates indicated above. At 2.5 mol/kg DMCHAH-HCO₃, the external mass transfer coefficient at 0.583 liter/minute is less than 1% lower than that at 1 liter/minute.

2.7. Reverse solute flux measurement

Samples were taken prior to every dilution of the draw solution, stored in glass vials sealed with PTFE tape, a PTFE-lined seal, an additional layer of PTFE tape, and parafilm, then stored in a refrigerator prior to shipment for analysis. Due to the partitioning of DMCHA into the

feed tank from which these measurements were taken, as evidenced by the smell of the amine in the dry tank even after being vacuum-dried at 70 °C, a long equilibration time (>2 hours) was allowed for the DI water feed at the start of each test to equilibrate with residual DMCHA and establish a baseline amine concentration for accurate tracking of reverse solute flux. Subsequently, DMCHA was not detected in any sample until after the membrane was exposed to draw solution, i.e. no partitioning of sorbed DMCHA into the feed from the feed tank was observed.

DMCHA concentration in the feed solution was quantified using gas chromatography (GC). GC analyses were carried-out using a HP (Agilent) 5890 GC equipped with a flame Ionization detector (FID). The GC column used in this work is a Restek®-Rtx-5, 30 m length, 0.25 mm ID, and 0.25 mm film thickness. Injections were made using an auto sampler with a 1 µl injection volume and a split ratio 10:1, the injection temperature was set to 250 °C. The oven program used: initial temperature set to 100 °C with a hold for 1 min then ramped to 200 °C at 15 °C /min with a final ramp to 300 at 50 °C /min. UHP helium was used as the carrier gas at a linear velocity of 30 cm/sec. The FID detector was held at constant 275 °C.

2.8. Desalination tests

The desalination potential of DMCHAH-HCO₃ was assessed using the aforementioned solvent tolerant FO system. The tests were run as a standard FO test as described in Section 2.6, however the feed volume was reduced from 4 liters to 3 liters to allow space for addition of sodium chloride solution. To ensure membrane integrity, a “blank” verification FO test was run versus DI water, followed by spiking the feed solution with sufficient 5 molar NaCl solution to increase the concentration to 0.50 molal, accounting for water flux across the membrane during the verification test.

Samples of feed were taken before the start of the test, after the verification test, and after the desalination test was complete, for analysis of DMCHA via the method described in Section 2.7. 25 mL samples of the draw solution were taken to analyze the salt rejection. These samples containing permeated salt were first boiled to dryness in glass vials. First a phase-separation occurs between DMCHA and water as CO_2 is removed. Eventually, the remaining DMCHA is removed via evaporation at high temperature. The residue (just sodium chloride) was suspended 25 mL of water yielding a clear, colorless solution.

The draw solution samples were analyzed for sodium and chloride content using techniques demonstrated previously[7,27]. Sodium analysis was done using direct aspiration atomic absorption spectrophotometry according to US EPA method 700B which has a lower detection limit of 0.002 mg/L and sensitivity of 0.015 mg/L for sodium[28]. These analyses were performed on a Thermo Scientific ICE 3000 atomic absorption spectrometer (Thermo Scientific, Nashua, New Hampshire) equipped with a combination potassium/sodium hollow cathode lamp, and samples were diluted if necessary. Chloride analysis was done using a modified Mohr titration[29]. Potassium chromate was added to the sample which was then titrated with silver nitrate. The endpoint of the titration is visible by a change in the color of the sample from yellow to reddish brown.

3. Results and Discussion

3.1 .Membrane stability

After up to 90 days of immersion in 10 mol/kg DMCHAH- HCO_3 , all membranes were observed to maintain selectivity to sodium chloride under brackish-water RO testing conditions. From the experimental analysis, three general trends were observed correlated to the type of membrane tested.

Figure 2: Reverse osmosis performance at 225 psi of commercial thin-film composite membrane after exposure to concentrated DMCHAH-HCO₃ draw solution. a) pure water permeance, b) sodium chloride permeability at 2000 ppm, c) intrinsic rejection at 2000 ppm.

The SW30HR seawater membranes were observed to have narrow distribution of both water permeance and sodium chloride permeability. However, an increase in hydraulic permeance was observed for these membranes after just a seven-day exposure to the concentrated DMCHAH-HCO₃. The SW30 and BW30 membranes both showed an inconclusive drop in solute rejection at the end of 90 days of exposure. Some SW30HR membranes had their

PET backing layers removed to ensure good contact between the support layer and DMCHA-HCO₃, better simulating an FO membrane. Previous studies in our lab[30] have not noted any significant decrease in selectivity or performance after removing a membrane from its backing layer. After exposure to concentrated DMCHA-HCO₃ solution, the average water permeance of the peeled SW30HR membranes was observed to oscillate above and below the value for the intact SW30HR membranes, potentially suggesting more variability, but ultimately showing the same behavior as the intact membranes.

The BW30 membrane, designed for brackish water RO, exhibited consistent water permeance and sodium chloride permeability for up to 60 days of exposure, but the membranes exposed for 90 days displayed large variability in both water permeance, more than any other membrane tested in this study. The BW30 membrane is targeted to be more permeable than the seawater SW30HR. It is likely this is accomplished by reducing the crosslink density of the selective layer on the BW30 membrane relative to the SW30. This hypothesis is supported by reported boron rejection, as mostly neutral boric acid at pH 8, for BW30 versus SW30HR modules[31] in which the BW30 membrane modules rejection 55-65% boron while SW30HR modules reject 90% boron.

The HTI TFC FO membranes exhibited a sharp increase in water permeance and a sharp decrease in selectivity after exposure for just 7 days. It should be noted that the HTI TFC membrane is designed for low pressure application in FO; however, HTI has publicized data of their TFC membrane operating at pressures of 150 psi[32]. The HTI TFC membrane exhibits reasonable performance compared to purpose-built RO membranes when not exposed to DMCHAH-HCO₃. While the membranes maintained reduced selectivity at longer exposure times, it is readily apparent that some degradation occurred. A viscous “slime” was observed to

slough off of the TFC membranes when they were removed from the DMCHAH-HCO₃ bath. To obtain good FO performance, the support layer of a membrane must be both thin and have a level of intrinsic hydrophilicity to achieve good wettability[33]. The addition of polyvinylpyrrolidone (PVP) is referenced in HTI's patent of this membranes[34]. PVP in particular, is soluble in amines[35], and thus is likely to be leached out by exposure to the DMCHAH-HCO₃ solution. This could very likely lead to performance degradation over long exposure times.

Since membranes are flushed with DI water under pressure before measuring their water permeance and solute permeability, it is not clear if sorption of neutral DMCHA into the selective layer could be a mechanism for the reduced selectivity of the HTI TFC and 90-day exposure BW30 membranes. In order for this mechanism to be plausible, the DMCHA would have to strongly associate with the polyamide selective layer. On the other hand, it is likely that DMCHA sorbed into the polysulfone support layer is not significantly desorbed either by immersion in pure water after exposure or by the convective flow through the pore space of the support layer during the flushing step. The swelling of the support layer could potentially lead to a loss of mechanical integrity, either by stretching and introducing defects in the adhesion between the selective layer and the support layer, or by collapsing under pressure. Pore collapse, which would lead to a decrease in water permeance, was not observed in this study. Given the performance of the SW30HR membranes with and without its PET backing layer, it is also apparent that any swelling of the polyester backing layer is not correlated to changes in membrane performance. Since no serious loss in integrity was observed for the RO membranes, it is unlikely that swelling of the polysulfone support layer will be a significant factor in designing an SPS-tolerant FO membrane.

3.2 DMCHAH-HCO₃ draw solute characterization

Despite the comparatively poor performance of the HTI TFC membrane under RO in long-term exposure studies, it was, at the time of the study, the only widely-available commercial TFC membrane available to universities for FO research. Thus it was chosen as a model membrane for studying the osmotic flux of DMCHAH-HCO₃ under FO and PRO-mode testing. Water flux in the PRO-mode was substantially lower than that measured by Stone et al[18] utilizing a cellulose triacetate membrane also provided by HTI and a DMCHAH-HCO₃ draw concentration of only 7.6 mol/kg. However cellulose acetate hydrolyzes due to the alkaline pH of the DMCHAH-HCO₃ solution, reported at 8.8, and likely swells in the presence of DMCHA as well.

The water flux under FO and PRO mode testing was almost insensitive to solute concentration, as shown in **Figure 3**. The diffusivity of DMCHAH-HCO₃, as an ionic pair, is roughly an order of magnitude less than that of sodium chloride (see supplemental information). Additionally, the viscosity of 10 mol/kg DMCHAH-HCO₃ in centipoise is approximately 15 times greater than that for pure water. The effective Reynolds and Schmidt number for the 10 mol/kg DMCHAH-HCO₃ solution are 40.8 and 852,000, respectively. Thus concentration-insensitive performance is, in large part, ascribable to the high viscosity of the solution and low diffusivity of the solute, which creates a mass transfer limitation on the draw side regardless of the concentration used.

Figure 3: a) Average water flux, b) average amine flux (dotted line), and c) average specific solute flux for DMCHAH-HCO₃ draw solute in FO and PRO mode.

Each data point for FO and PRO mode testing was taken after equilibration to ensure that the DMCHA, which is expected to have relatively slow diffusion through the selective layer due to its size, was given at least 60 minutes to form a steady-state ICP profile. No such change in water flux was observed while the reverse solute flux was observed both to be variable and high

compared to results with other tertiary amine draw solutes[36]. The minimum reverse solute fluxes, as neutral DMCHA, observed in FO and PRO were 95.3 and 129.3 mmol/m²hr respectively, while the maxima were 659.9 and 1280.7 mmol/m²hr. It is not certain what the cause for this wide range, without apparent change in water flux, might be. Since both the feed and draw solutions are exposed to the atmosphere, it is not feasible to monitor the crossover of carbonate species. Due to the high magnitude of reverse solute flux, it appears that DMCHA sorbs into the membrane as a neutral material, as the reverse solute flux of a large ion pair would be expected to be fairly low in the absence of ion-exchange phenomena. Studies on DMCHA have indicated a relatively constant ratio of DMCHA, neutral or charged, to bicarbonate ions at all concentrations, in which more DMCHA is present than bicarbonate ions[20]. Because of this, the concentration of neutral DMCHA species on the draw solution is elevated at high concentration, which could be, in part, an explanation for why the flux of DMCHA is so high.

Figure 4 demonstrates the relative magnitude of the external mass transfer coefficient modelled using **Equation 1** at the relevant concentrations at a reference flow rate of 1 liter/minute (~21 cm/s crossflow velocity) used on the feed side. As discussed previously, the mass transfer coefficients at the flow rates used in the experiment are not substantially different from this reference flow rate, e.g. the modelled mass transfer coefficient is not a strong function of crossflow velocity. Due to the lower diffusivity and higher viscosity of DMCHAH-HCO₃ solutions, transfer of DMCHAH-HCO₃ through the external boundary layer is much slower than that for sodium chloride. It should be noted that, from estimating the osmotic pressure of DMCHAH-HCO₃ draw solution, the interfacial concentration of DMCHAH-HCO₃ is substantially lower than that of the bulk draw solution for both FO and PRO mode operation. Consequently, due to the corresponding change in concentration of both solute and solvent, film-

theory, despite its successful application to many osmotic systems, may not be accurate, as the average molar velocity will change significantly as the molar concentrations of the transporting species undergo large changes, resulting in “weak” compressibility within the boundary layer[37].

Figure 4: Simulated mass transfer coefficients for DMCHAH-HCO₃ and sodium chloride in the test cell used in this work (flow area = 0.79 cm²).

3.3. Desalination performance of DMCHAH-HCO₃ draw solute

Despite the low flux and large variability in reverse solute flux in FO and PRO, the performance of DMCHAH-HCO₃ under desalination conditions was measured to show that the TFC membrane is capable of rejecting salt when used with the DMCHAH-HCO₃ draw solution. Notably, the flux of water against a 0.50 molal sodium chloride feed solution was, on average, almost unchanged from the water flux against pure water with an identical 10 molal DMCHAH-HCO₃ draw solution, as shown in **Table 1**. The flux of sodium and chloride were both extremely low, although the chloride measurement was more varied. This is in contrast to desalination using the ammonia-carbon dioxide draw solution which show sodium/ammonium cation exchange resulting in low cation rejection[7,8]. No such effect was observed here and the

individual rejection of sodium and chloride were found to be higher under 0.50 molal NaCl feed FO desalination than they were under 2000 ppm NaCl feed RO desalination, at approximately 98.8 (average of both ions) versus approximately 95%. This is observed despite the fact that a) reverse solute flux of the DMCHA was an order of magnitude higher and more variable than the NaCl flux, and b) the water flux in the RO desalination test was approximately 5 times that of the FO test. The lowest reverse solute flux measured during desalination tests was 75.3 mmol/m²•hr while the highest was 148.2 mmol/m²•hr.

Table 1: Desalination water flux and sodium chloride rejection of 10 molal DMCHAH-HCO₃ draw solute versus 0.5 mol/liter sodium chloride in FO mode. Data is average of three tests.

Water Flux [liter/m ² /hr]	Species	Solute Flux [mmol/m ² /hr]	% Rejection [%]
	Amine:	117.2 ± 37.64	~
7.20 ± 0.57	Sodium:	16.3 ± 7.8	99.5 ± 0.2
	Chloride:	72.5 ± 54.6	98.0 ± 1.3

Previously, Stone et al[18] demonstrated the rejection of dilute, uncharged DMCHA at its saturation concentration in water (ca. 18 g/liter at 25 °C) in a hand-powered seawater reverse osmosis system and measured it to be 99.65%. This result, along with many other studies of the rejection of organics and amines, would imply that the reverse solute flux of DMCHA would be much lower than it appears for this study. As previously mentioned, it is possible that DMCHA can degrade the polymer support used in the HTI TFC membrane. However, unless there are areas of support polymer exposed through the polyamide layer of the membrane, e.g. polyamide nodules spanning a pore mouth but leaving the area between pores exposed, it seems unlikely that membrane degradation could explain both the high NaCl rejection *and* high DMCHA flux. Further work will be required to determine the specific cause of the high reverse solute flux for DMCHA, however a reasonable hypothesis would be that the HTI TFC membrane has a less-

tightly crosslinked selective layer than the seawater desalination membrane used by Stone et al. While direction comparison is difficult, studies on HTI TFC membranes have indicated a boron rejection of approximately 45% in FO testing[38], which we offer as comparison to the high rejection of boron previously mentioned for the SW30HR membrane.

4. Conclusions

Despite some variability in membrane stability when subjected to the concentrated DMCHAH-HCO₃ draw solution, it appears reasonable that conventional membrane materials, such as those used in the preparation of the commercial seawater RO membranes, can be used to build a membrane optimized for performance in DMCHA-HCO₃ and other tertiary amine draw solutions. none of the seawater RO membranes experienced a large loss of salt selectivity after up to 90 days exposure to concentrated DMCHAH-HCO₃. Despite the comparatively low rejection of the HTI TFC membrane in RO testing (ca. 95%), paradoxically better desalination performance was obtained in FO, with no indication of any ion-exchange phenomena. Given that methods of improving FO membrane performance, such as coating or integrating hydrophilic materials into the support layer, may be incompatible with SPS draw solutes, it appears that an SPS-tolerant membrane should be designed with an FO-style open support layer, but a seawater RO-style active layer capable of higher rejection of neutral species. Further studies are necessary to determine if swelling of the support layer polymer is the cause of the reduced NaCl rejection of FO membranes in RO after extended exposure to DMCHAH-HCO₃ material as opposed to the unchanged rejection of RO membranes. In this case, higher molecular weight polysulfones, or alternative polymer supports may be necessary for long-term SPS-tolerance.

Glossary of terms

<i>NSh</i>	Sherwood number	(a.u.)
<i>NRe</i>	Reynolds number	(a.u.)
<i>NSc</i>	Schmidt number	(a.u.)
<i>dh</i>	Hydraulic diameter	(m)
<i>ℓ</i>	Length of flow channel	(m)
<i>k</i>	External mass transfer coefficient	(m/s)
<i>D</i>	Diffusion coefficient	(m ² /s)
<i>C_{bulk feed}</i>	Concentration of feed solution	(mol/L)
<i>C_{permeate}</i>	Concentration of permeate	(mol/L)
<i>C_{membrane}</i>	Concentration of feed at membrane interface	(mol/L)

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