Graphical Abstract

Performance Evaluation of Trimethylamine – Carbon Dioxide Thermolytic Draw Solution for Engineered Osmosis

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Abstract

We evaluated the performance of trimethylamine–carbon dioxide (TMA–CO₂) as a potential thermolytic draw solution for engineered osmosis. Water flux and reverse solute flux with TMA–CO₂ draw solution were measured in forward osmosis (FO) and pressure retarded osmosis (PRO) modes using thin-film composite (TFC) and cellulose triacetate (CTA) FO membranes. Water flux with the TMA–CO₂ draw solution was comparable to that obtained with the more common ammonia–carbon dioxide (NH₃–CO₂) thermolytic draw solution at similar (1 M) concentration. Using a TFC-FO membrane, the water fluxes produced by 1 M TMA–CO₂ and NH₃–CO₂ draw solutions with a DI water feed were, respectively, 33.4 and 35.6 L m⁻² h⁻¹ in PRO mode and 14.5 and 15.2 L m⁻² h⁻¹ in FO mode. Reverse draw permeation of TMA–CO₂ was relatively low compared to NH₃–CO₂, ranging from 0.1 to 0.2 mol m⁻² h⁻¹ in all experiments, due to the larger molecular size of TMA. Thermal separation and recovery efficiency for TMA–CO₂ was compared to NH₃–CO₂ by modeling low-temperature vacuum distillation utilizing low-grade heat sources. We also discuss possible challenges in the use TMA–CO₂, including potential adverse impact on human health and environments.

Keywords: Trimethylamine, Thermolytic, Draw Solution, Forward Osmosis, Engineered Osmosis

1. Introduction

Engineered osmosis collectively refers to membrane-based technologies that utilize osmotic pressure gradient as a driving force for water permeation across a semi permeable membrane [1, 2]. Engineered osmosis has the potential to produce fresh water from a variety of water sources (e.g., seawater, brackish water, or wastewater) by forward osmosis (FO) [3, 4], desalinate high-salinity brines from shale gas flowback water via FO coupled to a thermal separation [5, 6], and generate power from natural [7, 8] or anthropogenic salinity gradients [8, 9] by pressure-retarded osmosis (PRO). Because energy consumption in engineered osmosis arises from the separation and regeneration of the draw solution [9, 10], the selection of proper draw solutes is critical for energy-efficient process operation.

Thermolytic salts which exhibit phase change depending on the solution temperature represent an important class of draw solutes for engineered osmosis [10-13]. For a successful application in engineered osmosis, thermolytic draw solutes should produce high osmotic pressure, be strongly rejected by the membrane, and be amenable for thermal separation by low-temperature heat sources [9]. When low-grade heat sources, such as industrial waste heat or geothermal energy are available, operating costs associated with the draw solute thermal separation could be significantly reduced.

Ammonia-carbon dioxide ($\text{NH}_3\text{-CO}_2$) is currently the most successful thermolytic draw solution [9] and its technical feasibility has been demonstrated in laboratory experiments [12, 14], process modeling [15, 16], and more recently in a pilot-scale FO system operation [6]. Previous studies have shown that $\text{NH}_3\text{-CO}_2$ can generate high osmotic pressures to desalinate seawater [15] as well as high salinity produced water [6], and be separated at relatively low temperatures [15]. However, loss of draw solute by reverse permeation of draw solution species can be an operational challenge.

Amines have been widely used for CO_2 capture because an aqueous amine solution can absorb the CO_2 at ambient temperature and be regenerated by heat addition [17, 18]. Tertiary amines are known to have better thermal separation efficiency than primary and secondary amines [19] because they do not form stable carbamate during CO_2 absorption [20]. One particular tertiary amine — trimethylamine (TMA) ($\text{N}(\text{CH}_3)_3$) — has the potential to be used as thermolytic draw solution for engineered osmosis [21]. TMA features comparable volatility to

ammonia as indicated by its high Henry's law constant and low enthalpy of vaporization [22, 23]. In addition, reverse permeation and subsequent loss of TMA are expected to be lower than those of ammonia because the larger TMA molecule is better retained by the membrane in engineered osmosis.

In this study, we evaluate the performance of TMA-CO₂ as a potential draw solution for engineered osmosis. We first investigated the physiochemical and thermodynamic properties of TMA that are relevant to its potential use as a thermolytic draw solute. We then measured the water flux and reverse solute permeation with TMA-CO₂ draw solution in FO and PRO modes using two types of commercial FO membranes and compared the results to those obtained with NH₃-CO₂ draw solution at similar concentration. Required thermal energy for separation of TMA-CO₂ was analyzed by modeling low-temperature vacuum distillation utilizing low-grade heat and compared to NH₃-CO₂. The implications of the results for the use TMA-CO₂ for engineered osmosis are evaluated and discussed.

2. Materials and methods

2.1. FO membranes

Commercial thin-film composite FO (TFC-FO) membrane and cellulose triacetate FO (CTA-FO) membrane from Hydration Technology Innovation (HTI) were used for FO and PRO experiments. Both flat sheet membranes are specifically designed for osmotically-driven membrane processes, having substantially reduced support layer thickness compared to membranes used in pressure-driven processes (e.g., reverse osmosis). Prior to their use, membranes were immersed in 25% isopropanol solution for 30 min to allow complete wetting, and then rinsed with DI water. The pure water permeability coefficient, A , salt (NaCl) permeability coefficient, B , and structural parameter, S , were determined using laboratory-scale crossflow reverse osmosis (RO) and forward osmosis (FO) units. A detailed procedure of the FO membrane characterization is available in our previous studies [24, 25]. The determined properties (A , B , and S) of the FO membranes are provided in Table 1.

TABLE 1

2.2. Draw solutions

The properties of the draw solutions used in this study are summarized in Table 2. The performance of trimethylamine–carbon dioxide ($\text{N}(\text{CH}_3)_3\text{--CO}_2$) (TMA– CO_2) draw solution, evaluated by FO and PRO experiments, was compared with those of ammonia–carbon dioxide ($\text{NH}_3\text{--CO}_2$) and sodium chloride (NaCl) draw solutions. For a meaningful comparison, we employed the same molar ion concentration for all draw solutions. The pH, osmotic pressure, and viscosity of the draw solutions and the individual ion diffusivities were obtained using OLI Stream Analyzer (OLI Systems, Inc. Morris Plains, NJ). The mutual diffusion coefficients for draw solutes were determined from [26, 27]:

$$D_{\text{mutual}} = \frac{\frac{|z^+|}{D^+} + \frac{|z^-|}{D^-}}{\frac{|z^+|}{D^+} + \frac{|z^-|}{D^-}} \quad (1)$$

where z^+ and z^- are the cation/anion charges (+1/–1 for the draw solutions used), and D^+ and D^- are the individual cation/anion diffusivities, respectively.

A concentrated trimethylamine stock solution (25 wt % in water) was obtained from Sigma-Aldrich (St. Louis, MO, USA). To prepare the $\text{N}(\text{CH}_3)_3\text{--CO}_2$ draw solution, the stock solution was first diluted in deionized (DI) water to achieve the desired trimethylamine concentration. Carbon dioxide was then added to the trimethylamine solution by bubbling pure CO_2 gas (purity of 99.999%, Airgas). The amount of CO_2 injected was determined based on the solution pH as calculated from the OLI Stream Analyzer. Specifically, CO_2 gas was introduced to the trimethylamine solution until the solution pH reached 7.91 to form 1 M TMA– CO_2 solution (Table 2).

$\text{NH}_3\text{--CO}_2$ draw solution was prepared by dissolving ammonium bicarbonate salt (NH_4HCO_3) in DI water. To prevent degassing during mixing, small amounts of NH_4HCO_3 were added incrementally over time under gentle stirring. Temperature of the mixture was maintained at 25 °C.

TABLE 2

2.3. Measurement of water flux and reverse solute flux.

A laboratory-scale crossflow FO unit was used to measure the water flux and reverse solute flux. The experiments were performed in both FO (i.e., draw solution facing support layer) and PRO (i.e., draw solution facing active layer) configurations using DI water as a feed solution. All experiments were conducted for 1 hr with a crossflow velocity of 17.1 cm/s. Temperatures of both draw and feed solutions were maintained at 25 ± 0.5 °C.

Water flux, J_w , across the membrane was measured by monitoring the increase in draw solution mass at 1 min intervals. Data collected after the initial water flux had stabilized (always within 10 min) was averaged over a 50 min period. The draw solution concentration was assumed to be constant during the 1 hr experiment because the amount of permeate water causing the dilution of draw solution was low compared to the initial volume of the draw solution (i.e., 1.0 L). The reverse solute flux, J_s , was determined by measuring the total concentration of draw solute in the feed solution after the 1 hr experiment following the procedure described in our previous work [28]. Because the initial solute concentration in the feed is zero (DI water feed), a mass balance on the solute during FO or PRO run yields:

$$C_F(V_{F0} - J_w A_m t) = J_s A_m t \quad (2)$$

Here, C_F is the solute concentration in the feed after 1 hr experiments, V_{F0} is the initial volume of the feed solution, J_w is the average water flux, A_m is the membrane area, and t is the time.

Trimethylamine concentration in the feed solution was quantified using ion chromatography (IC; ICS-1000, Dionex, Sunnyvale, CA, USA). Separation of trimethylamine by IC was accomplished using Dionex Ionpac CS14 analytical column (250 mm length $\times$ 4 mm i.d.) with a Dionex Ionpac CG14 guard column (50 mm length $\times$ 4 mm i.d.). A 10 mM isocratic methanesulfonic acid was used as an eluent with a flow rate of 1.0 mL/min. Concentrations of NaCl, total ammonia, and total carbon species were measured using a conductivity meter (Oakton Instruments, Vernon Hills, IL), phenate method [29], and total organic carbon (TOC) analyzer (TOC-V, Shimadze Corp., Japan), respectively.

2.4. Modeling of water flux.

Water fluxes produced by TMA–CO₂, NH₃–CO₂, and NaCl draw solutions were compared to model prediction to better understand membrane performance with TMA. The following equations, which account for the effects of internal concentration polarization (ICP), external concentration polarization (ECP), and reverse draw solute permeation, were used for FO [30] (Eq. 3) and PRO [31] (Eq. 4) modes:

$$J_w^{FO} = A \left\{ \frac{\pi_{D,b} \exp\left(-\frac{J_w^{FO} S}{D}\right) - \pi_{F,b} \exp\left(\frac{J_w^{FO}}{k}\right)}{1 + \frac{B}{J_w^{FO}} \left[\exp\left(\frac{J_w^{FO}}{k}\right) - \exp\left(-\frac{J_w^{FO} S}{D}\right) \right]} \right\} \quad (3)$$

$$J_w^{PRO} = A \left\{ \frac{\pi_{D,b} \exp\left(-\frac{J_w^{PRO}}{k}\right) - \pi_{F,b} \exp\left(\frac{J_w^{PRO} S}{D}\right)}{1 + \frac{B}{J_w^{PRO}} \left[\exp\left(\frac{J_w^{PRO} S}{D}\right) - \exp\left(-\frac{J_w^{PRO}}{k}\right) \right]} \right\} \quad (4)$$

where $\pi_{D,b}$ and $\pi_{F,b}$ (equal to zero for DI water feed) are the draw and feed solution bulk osmotic pressures, respectively, k is the solute mass transfer coefficient, and D is the mutual diffusion coefficient of the draw solutes. The water permeability coefficient, A , and structural parameter of support layer, S , are intrinsic membrane properties. On the other hand, the draw solution bulk osmotic pressure, $\pi_{D,b}$, the mutual diffusion coefficient of the draw solutes, D , the solute mass transfer coefficient, k , and the solute permeability coefficient, B , are dependent on the type of draw solution. The water flux, J_w^{FO} or J_w^{PRO} , is the only unknown parameter in the equation, which can be solved by an iterative solution.

The solute mass transfer coefficients, k , were calculated from correlations for a rectangular cell geometry [32], and were determined to be 16.7, 17.0, and 15.3 $\mu\text{m/s}$ for NaCl, NH₃–CO₂, and TMA–CO₂ draw solutions, respectively. The solute permeability coefficients, B , for the different draw solutions were determined from PRO experiments by dividing the measured reverse solute flux, J_s , with the draw solute concentration at the membrane active layer surface [28]:

$$B = \frac{J_s}{C_{D,b} \exp\left(-\frac{J_w^{PRO}}{k}\right)} \quad (5)$$

where $C_{D,b}$ is the bulk concentration of draw solution and J_w^{PRO} is the experimentally determined PRO water flux. The solute permeability coefficients of TFC-FO and CTA-FO membranes for the NaCl, $\text{NH}_3\text{--CO}_2$, and TMA- CO_2 draw solutions are provided in Table 3.

TABLE 3

2.5. Modeling of thermolytic draw solution separation.

The thermal energy requirement for the separation of the thermolytic draw solutions was analyzed using a commercial chemical process modeling software (Aspen HYSYS[®], Cambridge, MA), in conjunction with an OLI electrolyte fluid package (Morris Plains, NJ). A single vacuum distillation system comprising a total-reflux stripping column, heat exchanger, condenser, reboiler, and circulation pump was used in HYSYS simulation as described in Fig. 1. The modeling results include the required heat duties for separation and regeneration of draw solute in the distillation column and the electrical power consumption by the circulation pump.

FIGURE 1

3. Results and discussion

3.1. Properties of trimethylamine-carbon dioxide draw solution

Trimethylamine-carbon dioxide (TMA- CO_2) draw solution is prepared by mixing two volatile gases in water. TMA and CO_2 are highly soluble in water, thereby creating high osmotic pressure. The osmotic pressure generated by TMA- CO_2 is comparable to that generated by NaCl (representative strong electrolyte draw solute), and higher than that created by $\text{NH}_3\text{--CO}_2$ (most common thermolytic draw solute) for similar ion concentrations (Table 2). In addition, TMA is relatively volatile, having high Henry's law constant and low enthalpy of vaporization (Table 4). Hence, thermal separation efficiency of TMA is expected to be as favorable as that of ammonia. Another key feature that renders TMA a potentially favorable draw solute compared to ammonia is its higher molecular weight (59.1 g/mol versus 17.0 g/mol for ammonia) and, hence, larger

molecular size. As we demonstrate later, reverse permeation of TMA is significantly lower compared to ammonia because the larger TMA molecule is better retained by the FO membrane.

Trimethylamine is a weak base and its speciation is dependent on the solution pH. When the solution pH is higher than its pK_a (9.87, Table 4), TMA mostly exists in an uncharged form in solution (i.e., $N(CH_3)_3$). In such a case, reverse TMA permeation would significantly increase due to the rapid transport of the uncharged species through the membrane. Addition of CO_2 decreases the solution pH, thereby altering the TMA speciation. Previous studies on CO_2 reaction with tertiary amines (e.g., TMA) in aqueous solution have shown that CO_2 does not directly react with tertiary amines [20, 33]. Instead, CO_2 combines with hydroxide and forms bicarbonate (HCO_3^-), which results in a decrease of the solution pH according to [33]:

Under conditions where the solution pH favors charged (protonated) species of TMA (i.e., $pH < pK_a$), TMA exists in a charged form of $NH(CH_3)_3^+$, and its reverse permeation is expected to be significantly reduced.

TABLE 4

3.2. Water flux produced by TMA- CO_2 draw solution

Water fluxes obtained from FO and PRO experiments using two types of FO membranes (i.e., TFC-FO and CTA-FO) are compared for TMA- CO_2 , NH_3 - CO_2 , and NaCl draw solutions (Fig. 2). TMA- CO_2 draw solution produced fairly high water flux when TFC-FO membrane was used while relatively lower water flux was obtained with CTA-FO membrane due to its much lower pure water permeability (Table 1). In most cases, except for PRO experiments with the CTA-FO membrane, water fluxes with TMA- CO_2 draw solution were slightly lower compared to those with NH_3 - CO_2 and NaCl draw solutions, although the calculated osmotic pressure for TMA- CO_2 draw solution was higher than the other two draw solutions (Table 2).

FIGURE 2

For a given membrane, water flux in FO or PRO is significantly hindered by the combined effect of internal and external concentration polarization (ICP and ECP, respectively), with ICP playing a much more prominent role [2, 34, 35]. The relatively lower water flux generated by the

TMA–CO₂ draw solution compared to NH₃–CO₂ and NaCl is attributed to the more pronounced effects of ICP and ECP contributed by the lower TMA solute diffusivity (Table 2). To verify the effects of solute diffusivity on the severity of ICP and ECP and the ensuing water flux for different draw solutions, we modeled water fluxes produced by TMA–CO₂, NH₃–CO₂, and NaCl draw solutions using Eqs. (3) and (4), and compared those values to the experimentally determined water fluxes. Modeled water fluxes were in good agreement with the experimentally measured water fluxes as presented in the Fig. 3.

FIGURE 3

3.3. Reverse Draw Solute Flux

Reverse permeation of TMA–CO₂ draw solution was determined by measuring the TMA concentration in the feed solution after 1 hr of FO and PRO experiments, and compared with those obtained with NH₃–CO₂ and NaCl draw solutions (Fig. 4). As hypothesized earlier, TMA was better rejected by the FO membrane than ammonia due to its relatively larger molecule size, resulting in a substantially reduced reverse draw solute permeation. Notably, the reverse permeation rates of cations (NH₄⁺ or NH(CH₃)₃⁺) and anions (HCO₃[−]) were almost identical for the TMA–CO₂ and NH₃–CO₂ draw solutions in both FO and PRO modes. Based on the solution-diffusion mechanism for transport in dense, salt-rejecting membranes like FO, the cations and anions pass through the membrane as a pair in order to maintain electro-neutrality [36, 37]. This mechanism explains the concomitant decrease in reverse permeation of HCO₃[−] in the FO and PRO experiments with TMA–CO₂ compared to experiments with NH₃–CO₂.

FIGURE 4

Reverse flux selectivity, defined as the ratio of forward water flux to reverse solute flux, is a key parameter determining the efficiency of draw solute [28]. Owing to a significantly reduced reverse draw solute permeation, TMA had a much higher reverse flux selectivity than ammonia as presented in Fig 5. Reverse flux selectivity for TMA was even higher than NaCl, which is a representative strong electrolyte draw solute used for diverse engineered osmosis applications [38-40]. The results suggest that TMA–CO₂ can be a viable thermolytic draw solute producing relatively high water flux and low reverse draw permeation.

FIGURE 5

3.4 Energy requirement for thermolytic draw solution regeneration.

To compare the heat duty required for the separation and reconcentration of TMA–CO₂ and NH₃–CO₂ draw solutions, a single, total-reflux distillation column (Fig. 1) operating under vacuum (10.54 kPa or 0.105 bar) was simulated with a dilute feed stream at a temperature of 60 °C to represent a low-grade heat source. HYSYS version 8.4 (a process simulation and optimization software from Aspen Technology Inc in Houston, TX) was used to model the distillation column and to calculate the energy requirements of the heat exchanger, reboiler, condenser, and flow circulating pump. The current version HYSYS employs a rate-based distillation model which uses mass and heat transfer correlations, depending on solution concentrations and transfer properties, to predict the performance of a distillation column. The rate-based modeling approach accounts for the concentration dependency of working fluids, thereby providing more accurate and realistic analysis on column separation [41, 42].

We used the same concentrations for draw solution streams fed to the FO/PRO module as those used in our FO and PRO experiments (i.e., 1 M of TMA–CO₂ or NH₃–CO₂). Dilution of the draw solution stream by FO or PRO was assumed to be 20%. This diluted stream is heated via heat exchanger (representing the low-grade heat source) before entering the distillation column. The distillation column comprises 12 stages (including the condenser and reboiler) and is designed to separate the draw solution into a concentrated stream (column tops) and diluted stream (column bottoms) containing <0.1 mM TMA or NH₃ and <0.1 mM HCO₃[–]. The feed stream enters the distillation column at the fifth stage.

In the simulation of the distillation process, the heat exchanger energy requirement to heat up the feed stream from 20 °C to 60 °C was calculated by HYSYS. Moreover, the final solute concentration in the product water (bottoms of the distillation column) was specified while the heat duties for the reboiler and condenser and the amount of product water were calculated and optimized by HYSYS. The modeling results indicate that thermal energy (expressed as heat duty per m³ of feed water) required for TMA–CO₂ recovery was 254 MJ/m³, which is lower than that required for NH₃–CO₂ recovery (397 MJ/m³) with supplied heat of 60 °C. We note that the thermal energy required for draw solution recovery is defined as a sum of heat input to the heat exchanger and reboiler minus the heat recovered from the condenser. The HYSYS calculated electrical duty needed for pumping the stream in the separation system was relatively negligible

(i.e., 6.20 and 6.68 kJ/m³ for TMA–CO₂ and NH₃–CO₂, respectively) compared to the heat duties of the heat exchanger, condenser, and reboiler. The relatively lower required heat for TMA–CO₂ recovery is attributed to the thermodynamic properties of TMA, namely the high Henry's law constant and low enthalpy of vaporization (Table 4). Because energy consumption in engineered osmosis arises primarily from the regeneration of draw solution [12, 15], the reduced energy requirement for recovery of the TMA–CO₂ draw solution allows leveraging low-grade heat sources typically available in many industrial settings.

3.5 Operational and health challenges of using TMA–CO₂ draw solution

Our experimental and modeling results demonstrated good performance of the TMA–CO₂ thermolytic draw solution. However, several challenges need to be further investigated and overcome for a successful application of TMA–CO₂ draw solution in engineered osmosis. Due to its high volatility, TMA has an extremely low odor threshold ranging from 0.00011 to 0.00058 ppm [43-46], which can incur significant odor problems during the process operation. Studies on human toxicity of TMA are limited because of its potentially hazardous impact on human health. Report from the American Industrial Hygiene Association (AIHA) indicated that no toxic effects were found in people who are chronically exposed to relatively low TMA concentrations (i.e., ranging from 0.1 to 8 ppm) [47]. However, acute exposure to TMA (i.e., >100 ppm) has been reported to cause irritation of the nose and throat, violent sneezing, pulmonary congestion, larynx constriction, and lung edema [48]. Considering TMA extremely low odor threshold, pungent fishy odor, and toxicity, rigorous and thorough care must be taken to limit human exposure to TMA when handling TMA–CO₂ draw solution. Such problems may limit the potential use of TMA–CO₂ draw solution in some industrial applications.

4. Conclusion

We evaluated the performance of trimethylamine–carbon dioxide (TMA–CO₂) draw solution using thin-film composite and cellulose triacetate FO membranes. Water flux and reverse solute flux with the TMA–CO₂ draw solution were measured in FO and PRO modes and compared to those with the more common NH₃–CO₂ thermolytic draw solution. TMA–CO₂ draw solution

produced comparable water flux to $\text{NH}_3\text{-CO}_2$ draw solution. However, water flux with the TMA- CO_2 draw solution was more hampered by the effects of ICP and ECP than $\text{NH}_3\text{-CO}_2$ because of the lower TMA diffusivity. Reverse draw solute permeation of TMA- CO_2 was lower than that of $\text{NH}_3\text{-CO}_2$ because of the larger TMA molecular size. Modeling results indicate that TMA- CO_2 draw solution could be separated and recovered at lower thermal energy consumption than $\text{NH}_3\text{-CO}_2$ using a low-temperature, vacuum distillation column. Potential environmental and health challenges associated with the use of the TMA- CO_2 draw solution were also discussed.

The performance of TMA- CO_2 demonstrated by our experiment as well as the modeling results is promising. However, the use TMA- CO_2 as a draw solution for engineered osmosis will should be limited to industrial applications where the TMA residual in the final product is of significantly less concern with regard to human health and the environment. Treatment of high salinity brine, such as those from shale gas operations and power plants, and sustainable power production by closed-loop osmotic heat engine with PRO, are possible industrial applications of TMA- CO_2 draw solution.

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Table 1. Properties of FO membranes as determined from reverse osmosis (RO) and forward osmosis (FO) characterization.

Membrane	Water Permeability Coeff., A ($\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$)	Salt (NaCl) Permeability Coeff., B ($\text{L m}^{-2} \text{h}^{-1}$)	Structural Parameter, S (μm)
HTI-TFC	3.16 ± 0.08	0.55 ± 0.03	553 ± 21
HTI-CTA	0.87 ± 0.13	0.51 ± 0.01	454 ± 36

Table 2. Properties of draw solutions compared in this study at 25 °C.

Draw Solution	Recipe	^a pH	^a Osmotic Pressure (bar)	^a Viscosity (cP)	^a Diffusivity (m ² /s)	^b Mutual Diffusion Coefficient (m ² /s)
NaCl	NaCl (1.0 M)	6.99	48.0	0.98	Na ⁺ : 1.18×10^{-9} Cl ⁻ : 1.74×10^{-9}	1.41×10^{-9}
NH ₃ -CO ₂	NH ₄ HCO ₃ (1.0 M)	7.52	40.1	1.03	NH ₄ ⁺ : 1.93×10^{-9} HCO ₃ ⁻ : 1.16×10^{-9}	1.45×10^{-9}
TMA-CO ₂	N(CH ₃) ₃ (1.0 M) + CO ₂ (1.0 M)	7.91	48.8	1.04	NH(CH ₃) ₃ ⁺ : 1.45×10^{-9} HCO ₃ ⁻ : 1.09×10^{-9}	1.24×10^{-9}

^aData from OLI software^bCalculated using Eq. (1)

Table 3. Solute permeability coefficients for NaCl, NH₃–CO₂, and TMA–CO₂ draw solutions determined from PRO experiments.

Membrane	Solute Permeability Coefficient, B (L m ⁻² h ⁻¹)		
	NaCl	NH ₃ –CO ₂	TMA–CO ₂
TFC-FO	0.71	1.21	0.54
CTA-FO	0.54	0.73	0.31

Table 4. Physical and thermodynamic properties of ammonia and amine compounds. Ammonia (NH₃) and trimethylamine ((CH₃)₃N) were used in this investigation.

Compound	Molecular Formula	Chemical Structure	Molecular Weight (g/mol)	^a Boiling Point (°C)	^b Enthalpy of Vaporization ΔH_v at the Boiling Point at 1.0 atm (kJ/mol)	^c Henry's Law Constant $K_{H,inv}^{Px}$ (Pa)	^d pK _a	^e Vapor Pressure at 25°C (kPa)
Ammonia	NH ₃		17	-33.34	23.33	9.71×10^4	9.25	1003
Methylamine	CH ₃ NH ₂		31.06	-6.7	25.6	8.64×10^4	10.64	306.64
Dimethylamine	(CH ₃) ₂ NH		45.08	7.4	26.4	1.40×10^5	10.64	195.98
Trimethylamine	(CH ₃) ₃ N		59.11	3.5	22.94	5.86×10^5	9.87	223.98
Ethylamine	C ₂ H ₅ NH ₂		45.08	16.6	27.5	9.55×10^4	10.7	20.40
Diethylamine	(C ₂ H ₅) ₂ NH		73.14	55.5	29.06	1.88×10^5	11.09	31.46
Triethylamine	(CH ₃ CH ₂) ₃ N		101.19	89.4	31.01	8.40×10^5	10.75	7.88
Isobutylamine	(CH ₃) ₂ CHCH ₂ NH ₂		73.14	68-69	30.61	9.12×10^5	10.68	18.67
sec-Butylamine	C ₂ H ₅ CH(NH ₂)CH ₃		73.14	66	29.92	N/A	10.56	23.33
tert-Butylamine	(CH ₃) ₃ CNH ₂		73.14	45.2	28.27	N/A	10.68	47.46
n-Butylamine	C ₂ H ₅ CH ₂ CH ₂ NH ₂		73.14	77.8	31.81	N/A	10.59	12.63
Isopropylamine	(CH ₃) ₂ CHNH ₂		59.11	33-34	27.83	7.72×10^4	10.63	78.93
Propylamine (n-Propylamine)	CH ₃ CH ₂ CH ₂ NH ₂		59.11	49-50	29.55	N/A	10.67	41.46

^aPerry's chemical engineers' Handbook, 8th edition

^bCRC Handbook of Chemistry and Physics

^cSander, R. (1999). Compilation of Henry's law constants for inorganic and organic species of potential importance in environmental chemistry

^d<http://www.zirchrom.com/organic.htm>

^eEstimation Programs Interface (EPI) developed by the US Environmental Protection Agency's Office of Pollution Prevention and Toxics and Syracuse Research Corporation (SRC)

Figure Captions

Fig. 1. Flow diagram of distillation column simulated using HYSYS (Rev. 8.4) for separation and regeneration of the thermolytic draw solutions ($\text{NH}_3\text{--CO}_2$ and TMA--CO_2).

Fig. 2. Water flux obtained from experiments with CTA-FO (green bar with diagonal pattern), and TFC-FO (blue bar with checked pattern) membranes in (a) FO mode and (b) PRO mode. Experiments were conducted for 1 hr using DI water as a feed solution and 1 M NaCl , $\text{NH}_3\text{--CO}_2$, or TMA--CO_2 as a draw solution. Crossflow velocity was set at 17.1 cm/s, and temperature was maintained at 25 ± 0.5 °C for both feed and draw solutions. All experiments were conducted in triplicate and the error bars represent one standard deviation.

Fig. 3. Experimentally measured (blue open circles) and modeled (green open triangles) water fluxes for NaCl , $\text{NH}_3\text{--CO}_2$, and TMA--CO_2 draw solutions. Modeled water flux was calculated using Eq. (3) for FO mode and Eq. (4) for PRO mode, respectively. Calculations were done for draw and feed solution temperatures at 25 °C and cross flow velocities of 17.1 cm/s.

Fig. 4. Reverse draw solute flux obtained from experiments with (a) TFC-FO membrane in FO mode, (b) TFC-FO membrane in PRO mode, (c) CTA-FO membrane in FO mode, and (d) CTA-FO membrane in PRO mode. The experiments were conducted for 1 hr using DI water as a feed solution and 1 M NaCl , $\text{NH}_3\text{--CO}_2$, or TMA--CO_2 as a draw solution. Crossflow velocity was set at 17.1 cm/s, and temperature was maintained at 25 ± 0.5 °C for both feed and draw solutions.

Fig. 5. Reverse flux selectivity of TFC-FO and CTA-FO membranes for NaCl , NH_4^+ , and $\text{NH}(\text{CH}_3)_3^+$ in (a) FO mode and (b) PRO mode. The reverse flux selectivity was calculated by dividing the water flux (data presented in Fig. 2) with the reverse solute flux (data presented in Fig. 4).

Fig. 1. Flow diagram of distillation column simulated using HYSYS (Rev. 8.4) for separation and regeneration of the thermolytic draw solutions ($\text{NH}_3\text{-CO}_2$ and TMA-CO_2).

Fig. 2. Water flux obtained from experiments with CTA-FO (green bar with diagonal pattern), and TFC-FO (blue bar with checked pattern) membranes in (a) FO mode and (b) PRO mode. Experiments were conducted for 1 hr using DI water as a feed solution and 1 M NaCl, $\text{NH}_3\text{-CO}_2$, or TMA- CO_2 as a draw solution. Crossflow velocity was set at 17.1 cm/s, and temperature was maintained at 25 ± 0.5 °C for both feed and draw solutions. All experiments were conducted in triplicate and the error bars represent one standard deviation.

Fig. 3. Experimentally measured (blue open circles) and modeled (green open triangles) water fluxes for NaCl, $\text{NH}_3\text{-CO}_2$, and TMA- CO_2 draw solutions. Modeled water flux was calculated using Eq. (3) for FO mode and Eq. (4) for PRO mode, respectively. Calculations were done for draw and feed solution temperatures at 25 °C and cross flow velocities of 17.1 cm/s.

Fig. 4. Reverse draw solute flux obtained from experiments with (a) TFC-FO membrane in FO mode, (b) TFC-FO membrane in PRO mode, (c) CTA-FO membrane in FO mode, and (d) CTA-FO membrane in PRO mode. The experiments were conducted for 1 hr using DI water as a feed solution and 1 M NaCl, NH₃-CO₂, or TMA-CO₂ as a draw solution. Crossflow velocity was set at 17.1 cm/s, and temperature was maintained at 25 ± 0.5 °C for both feed and draw solutions.

Fig. 5. Reverse flux selectivity of TFC-FO and CTA-FO membranes for NaCl, NH₄⁺, and NH(CH₃)₃⁺ in (a) FO mode and (b) PRO mode. The reverse flux selectivity was calculated by dividing the water flux (data presented in Fig. 2) with the reverse solute flux (data presented in Fig. 4).