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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–CO_2) as a potential thermolytic draw solution for engineered osmosis. Water flux and reverse solute flux with TMA–CO_2 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–CO_2 draw solution was comparable to that obtained with the more common ammonia–carbon dioxide (NH_3–CO_2) thermolytic draw solution at similar (1 M) concentration. Using a TFC–FO membrane, the water fluxes produced by 1 M TMA–CO_2 and NH_3–CO_2 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–CO_2 was relatively low compared to NH_3–CO_2, 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–CO_2 was compared to NH_3–CO_2 by modeling low-temperature vacuum distillation utilizing low-grade heat sources. We also discuss possible challenges in the use TMA–CO_2, including potential adverse impact on human health and environments.

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 (NH_3–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 NH_3–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) ($N(CH_3)_3$) — 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

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TMA molecule is better retained by the membrane in engineered osmosis.

In this study, we evaluate the performance of TMA–CO_2 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–CO_2 draw solution in FO and PRO modes using two types of commercial FO membranes and compared the results to those obtained with NH_3–CO_2 draw solution at similar concentration. Required thermal energy for separation of TMA–CO_2 was analyzed by modeling low-temperature vacuum distillation utilizing low-grade heat and compared to NH_3–CO_2. The implications of the results for the use TMA–CO_2 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 shown in Table 1.

2.2. Draw solutions

The properties of the draw solutions used in this study are shown in Table 2. The performance of trimethylamine–carbon dioxide ($N(CH_3)_3$–CO_2) (TMA–CO_2) draw solution, evaluated by FO and PRO experiments, was compared with those of ammonia–carbon dioxide (NH_3–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]:

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

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 $N(CH_3)_3$–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).

NH_3–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.

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 h 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

Table 1

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

Membrane	Water permeability coeff., A ($L\,m^{-2}\,h^{-1}\,bar^{-1}$)	Salt (NaCl) permeability coeff., B ($L\,m^{-2}\,h^{-1}$)	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	pH[a]	Osmotic pressure (bar)[a]	Viscosity (cP)[a]	Diffusivity (m^2/s)[a]	Mutual diffusion coefficient (m^2/s)[b]
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_4HCO_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}

[a] Data from OLI software.

[b] Calculated using Eq. (1).