Membrane Compatibility with Switchable Polarity Draw Solutions for use in Forward Osmosis Applications

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ABSTRACT: Water scarcity is a problem being faced worldwide and present in every continent. Close to one-fifth of the world’s population has difficulty acquiring safe water, and the problem is worsening as populations continue to grow in poorer countries. As the availability of unimpaired freshwater sources dwindle, water sources, such as the oceans and saline ground waters, must be tapped. However, desalination technologies are very expensive due to a high energy requirement. Forward osmosis (FO) is a process which may be able to replace or become integrated with existing desalination technologies like reverse osmosis. FO relies on an osmotic agent, or draw solution, to drive water from a saline water source by osmosis. The water dilutes the draw solution and a secondary separation process removes solutes and recycles the draw solution. This secondary separation step is key to FO process economics. Recently, a classification of draw solutes, known as switchable polarity solvents (SPSs) have emerged. These solvents become highly miscible with water upon sparging with CO₂ and phase separate when stripped with an inert gas. One such SPS is N,N-dimethylcyclohexylamine. This SPS has shown promise in early testing at Idaho National Laboratories. However, because it is a solvent, membranes, which are polymeric, may not be compatible with the solution. This study examines the longevity of conventional osmotic membranes after exposure to relevant SPS solutions. Membrane performance metrics, such as permeance and salt rejection as well as osmotic flux, are presented.
1 Introduction

Water scarcity affects every continent. 1.2 billion people live in areas where water is scarce with an additional 500 million nearing these conditions. Additionally, 1.6 billion people, nearly one quarter of the world, lack required infrastructure to draw water from rivers and aquifers. With water usage growing at more than twice the rate of population increase, it is necessary to find an economically feasible way to satisfy the world’s demand for water [1]. Reverse Osmosis (RO) is a prominent and electricity intensive method of desalinating water which only recovers about 35-50 % of the feed water. Forward Osmosis (FO) is an emerging technology which is capable of desalinating water at much lower costs.

1.1 Osmosis and Osmotic Pressure

Osmosis refers to the movement of water with a high chemical potential through a semipermeable membrane into a solution of lower water chemical potential. This action equalizes chemical potential on either side of the membrane. The main driving force is a difference in solute concentration across the membrane. The membrane rejects most solutes, allowing only water to pass, diluting a concentrated solution [2].

When enough pressure is applied to a solution, spontaneous transport of water across the membrane can be stopped. This pressure is referred to as the osmotic pressure. The typical way to calculate osmotic pressure is by use of the Van’t Hoff equation:

\[ \pi = \varphi i M R T \]  

where \( \pi \) is the osmotic pressure, \( M \) is the molarity of the solution, \( R \) is the universal gas constant, \( T \) is absolute temperature, ‘\( i \)’ is the dissociation constant corresponding to the number of species into which a solute can dissociate, and \( \varphi \) is a Van’t Hoff coefficient which is a tabulated value specific to different non-ideal solutions.

1.2 Forward Osmosis

Two solutions present with different osmotic pressures have a natural tendency for water to travel into the solution with a higher osmotic pressure. This continues until there is no difference in osmotic pressure, \( \Delta \pi \). This process is called Forward Osmosis. The flux of water from the low osmotic pressure solution is proportional to the osmotic pressure and can be characterized using equation (2):

\[ J_w = A \Delta \pi \]  

where \( J_w \) is water flux and \( A \) is the permeance, also called the water permeability coefficient.

FO is an emerging technology for water purification rivaling its energy intensive counterpart, RO. A general FO process is represented in Figure 1.

![Figure 1. A general representation of an FO process. An FO cell separated by a semipermeable membrane allows flux of water from a feed solution into a draw solution. Potable water can be separated from the draw solution and draw solution can be recycled. Figure adapted from [8].](image-url)
A feed solution such as brine is fed to a system containing an FO cell. Two halves of the cell are separated by a semipermeable membrane. A draw solution is present on the opposite side of the membrane having a high osmotic pressure. Water from the feed solution is driven through the membrane by the osmotic pressure gradient, diluting the draw solution. A method, specific to the draw solution, is used to separate water yielding potable water and a regenerated draw solution.

1.2.1 Draw Solutions
Theoretically, any solution that can attain a higher osmotic pressure than a feed solution can be used as a draw solution. However, if a draw solution is to be used for water purification purposes, it must exhibit high osmotic efficiency, be chemically compatible with membranes, and be easily and economically separated and recycled. [3] Without these criteria working in harmony, the process will not be viable. A number of draw solutions have been proposed and tested.

Batchelder suggested volatile solutes such as sulfur dioxide \((SO_2)\) which can be driven off by heating. [4] Glew took this idea further by using a two phase liquid system. The system is made of an extracting agent such as \(SO_2\) or aliphatic alcohols. One phase is rich in water while the other is rich in extracting agent. The phase rich in water is used as the draw solution. As FO occurs, extracting agent from the extracting agent-rich phase is transferred to the water-rich phase keeping a constant composition rather than suffering dilution. The two phases can then be separated continuously or periodically. The extracting agent is readily removed from the separated water-rich phase by flash distillation or conventional distillation. [5]

Frank suggested the use of precipitable salts such as aluminum sulfate or magnesium sulfate. Osmotic pressure is maintained in the draw due to an excess of soluble salt which is diluted by feed water. In subsequent steps, all salts are precipitated and separated. Further purification yields clean water. [6]

McGinnis took advantage of the temperature dependent solubility of solutes. Potassium nitrate \((KNO_3)\) has a solubility directly related to temperature while sulfur dioxide \((SO_2)\) has a solubility inversely related to temperature. Because sodium chloride is difficult to remove from water, a series of intermediate solutions are used for separation. Dissolved \(KNO_3\) in a high temperature solution draws water from the feed solution through forward osmosis. It is cooled, precipitating \(KNO_3\), and sent to a second forward osmosis chamber where highly concentrated \(SO_2\) is diluted by feed water. The \(SO_2\) solution is then heated, driving off dissolved \(SO_2\) leaving a potable water solution. [7]

McCutcheon et al. describes a method of using an ammonia-carbon dioxide draw solution. Ammonium bicarbonate is dissolved in water making the draw solution. After the process, moderate heating decomposes the bicarbonate allowing a low temperature distillation separation of carbon dioxide and ammonia, yielding potable water. The draw solution reached osmotic pressures far greater than seawater allowing for high water flux and recovery. [8]

Ling et al. are among the first to systematically investigate the use of magnetic nanoparticles as a draw solution. Fine magnetic nanoparticles were functionalized using 2-pyrrolidone, triethylene glycol and polyacrylic acid
using a thermal decomposition synthesis. The synthesized molecules are highly soluble in water. Flux during FO testing was relatively low but it is believed that this could be increased by surface modification and by decreasing the diameter of the magnetic nanoparticles. After FO testing, the particles can be removed using a magnetic field. [9]

Comestible draw solutions have gained a great deal of attention. This takes away the separation step as the draw solution is a part of the final product. Kravath et al. use a hypertonic glucose solution as draw solution. [10] Stache invented an elongated flexible housing with an interior separated from a concentrated fructose solution by a semipermeable membrane. When filled with water, clean water dilutes the fructose. Fructose generates a high osmotic pressure and does not produce thirst within the human body making it a convenient and edible draw solution. [11]

The preceding methods (with the exception of comestible draw solutions) share a theme of generating high osmotic pressures and having the ability to separate the draw solute from the product water. When searching for a new draw solution for water purification applications, it is important to consider these qualifications as they will dictate the process.

1.2.2 N,N-dimethylcyclohexylamine as a draw solution
The draw solution investigated in this paper is a tertiary amine called N,N-dimethylcyclohexylamine which is immiscible in water. When protonated, it becomes water miscible. N,N-dimethylcyclohexylamine is labeled as a switchable polarity solvent (SPS) due to these properties. The switching process follows the reaction shown in Figure 3.

\[
NR_3 + CO_2 + H_2O \leftrightarrow HNR_3^+ + HCO_3^{-}
\]

Figure 3. A general example of an SPS switching reaction. NR3 is water immiscible while HNR3+ is water miscible

Using an SPS as a draw solution is appealing due to high osmotic efficiency and the ability to recycle and remove trace amounts from product. It exhibits high osmotic efficiency due to high osmotic pressures obtained in its hydrophilic form. A fully concentrated solution has been reported at 13.3 Osm/kg [12]. This is theoretically greater than a fully concentrated brine solution, meaning there will still be positive flux even at high feed concentrations [12]. The mechanism for separation is shown in Figure 4.

SPS in its hydrophilic form is used as the draw solution. After FO is run, the SPS is left dilute. By removing CO2 from solution, the reaction in Figure 3 reverses, leaving a hydrophobic amine layer and water. CO2 is stripped from solution by bubbling an inert gas such as argon or nitrogen through the solution. The water can be separated and purified further, if necessary, using a process such as reverse osmosis (RO). The draw solution is then regenerated by sparging the hydrophobic SPS with CO2.

![Figure 2: Structure of N,N-dimethylcyclohexylamine](image-url)
A SPS such as N,N-dimethylethanolamine thus satisfies two of the three properties described above for an acceptable draw solution. It has a high osmotic efficiency (generates a high osmotic pressure) and has an easy method for recycling. The final criteria to be evaluated is that of its membrane compatibility. This is evaluated in the remainder of this paper. Testing compatibility with current commercial membranes is essential to the success of this SPS as a draw solution. Experiments were run to test the long term effects of membrane exposure to the SPS in its hydrophilic form. Membranes were characterized after exposure using reverse osmosis.

1.3 Reverse Osmosis

A bench scale reverse osmosis (RO) system was used to characterize membrane performance. During RO, pressure is applied to the feed solution against the osmotic pressure gradient. This reverses the direction of water flux, concentrating the solution as the semipermeable membrane rejects dissolved solutes. The resulting permeate becomes the product [13]. Figure 5 illustrates this process in general.

\[
J_w = A(\Delta P - \Delta \pi) \quad (3)
\]

Because \( \Delta \pi \) now opposes water flux, it is subtracted from the applied pressure. The water permeability coefficient, \( A \), is calculated using this equation.

Another parameter to be measured is salt rejection. Different membranes have varying abilities to reject solutes. It is calculated using equation (4):

\[
\%R = \left(1 - \frac{c_p}{c_F}\right) \times 100\% \quad (4)
\]
where \( C_P \) is the concentration of the permeate and \( C_F \) is the concentration of the feed solution at the membrane interface.

A third parameter describes solute flux. \( B \) is the solute permeability coefficient calculated using

\[
B = \frac{(1-R)J_w}{R} \tag{5}
\]

where \( J_w \) is calculated using equation (2) and \( R \) is rejection (note: not percent rejection) \([2]\).

In this study it will be determined whether exposure to SPS has any negative effect on \( A \), \( B \) or \( R \), gaging membrane tolerance.

1.4 Chosen Membranes

FO progress has been slow due to an absence of effective membranes. Most FO-specific membranes are still under laboratory investigation. This usually limits FO studies to membranes designed for RO \([14]\). The SW30HR and BW30 membranes are both RO membranes which will be studied. Fortunately, Hydration Technology Innovations (HTI) has released a membrane specifically for FO called the HTI-TFC which will also be studied. These membranes are chosen because they are commercially available and have potential to be chemically resistant to the SPS. If the membranes are compatible with the SPS, this makes the process viable for industry. Their compatibility is not trivial and requires a thorough characterization.

The chosen membranes are all asymmetric thin film composite (TFC) membranes. TFC membranes have largely replaced cellulose acetate based membrane because of their superior separation properties and excellent pH stability \([15]\). They are made of three layers of different polymers with different thicknesses shown in Figure 6.

![Figure 6: The three layers which make up the thin film composite membranes used in these studies. From top to bottom: Polyamide, Polysulfone, and Polyester](image)

A thin selective polyamide layer is synthesized on top of a spongy polysulfone substrate via interfacial polymerization. A polyester support layer is attached to the previous layers providing mechanical strength. In the RO membranes, the polyester layer may be compact and thick due to high pressures encountered. FO membrane polyester supports tend to have a finger-like porous structure \([16]\). In the case of the HTI-TFC membrane, polyester fibers are embedded in a mesh eliminating the need for a thick porous support layer \([14]\).

1.4.1 Polymer Degradation

To justify the testing of the three chosen membranes, it is necessary to understand what can cause degradation of each polymer. If the chosen SPS is speculated to react negatively with any layer of the membranes, then there is no point investigating. The general structure for each polymer is given in Table 1.

Swelling is a phenomenon which occurs as solvent molecules slowly diffuse into
the polymer producing a swollen gel. If forces between the polymer are not strong, polymer-solvent interactions might dominate causing polymer degradation. High polymer-polymer forces caused by crosslinking, crystallinity and hydrogen bonding help to prevent degradation by solvent. The actions take place usually minimizing Gibbs energy of mixing of the polymer-solvent system. Generally membrane transport can be effected in two directions due to swelling. Diffusivity of components can increase or decrease based on interactions of different molecular species within the polymer [17].

To speculate how the three layers might interact with the SPS, trends were found between solvents which are able to dissolve the polymers.

Polyamides (synonymous with nylon) are resistant to oils, greases, lubricants, and hydrocarbons along with most other chemicals. Phenols, strong acids and oxidizing agents such as chlorine will cause degradation. Polyamides generally operate at a wide pH range and are less susceptible to hydrolysis than previously studied cellulose acetate membranes [18]. The SPS is not a phenol, strong acid or oxidizing agent and should not pose a threat to this layer.

Polysulfone is resistant to surfactants, hydrocarbon oils, non-polar solvents, mineral acids, and oxidizing agents. They are very resistant to hydrolysis. Ketones, chlorinated hydrocarbons and aromatic hydrocarbons will readily dissolve polysulfone. Some common solvents include dimethylformamide, N-methylpyrrolidone, dichloromethane and chlorobenzene [19]. The SPS is not a ketone, chlorinated or aromatic and should not affect the polysulfone.

Polyesters generally undergo reactions typical of alcohols. They are largely dictated by the behavior of terminal hydroxyl groups. Polyesters are relatively sensitive to hydrolysis. Reaction of a polyester with an alcohol can lead to newly formed acidic groups which exhibit an autocatalytic effect, breaking the polymer into diols and dicarboxylates [20]. The SPS should not play any significant role in catalyzing hydrolysis of the polyester layer.

Membrane stability studies are justified because there are no significant signs of negative solvent interaction with the membrane material. Swelling is likely and its effects may be observed during experimental studies.

2 Experimental
2.1 Materials
N,N-dimethylcyclohexylamine (MW 127.23, 99%) was purchased from Acros Organics. Deionized water was obtained
using an Elix ultrapure water purification system (Millipore, Billerica, MA). Commercial asymmetric thin film composite (HTI-TFC) FO membrane (Hydration Technology Innovations Inc., Albany, OR), and RO thin film composite membranes (SW30HR, BW30) (The DOW Chemical Company) were acquired for exposure and characterization.

2.2 Preparation of SPS and membrane exposure

N,N-dimethylcyclohexylamine, as received, is in its hydrophobic form. During FO testing, the membranes will only be exposed to the switched, hydrophilic form. To perform an accurate exposure study, it was necessary to switch the SPS. This was done using a batch process as shown in Figure 7. A 2 liter, glass vessel was used. To this, an equal amount, by mass, of SPS and Elix water were added. The solution was stirred using a magnetic stir bar, and sparged with carbon dioxide. Operation was performed under a fume hood at all times. The reaction goes to completion taking between 3 and 6 hours depending on the sparge rate and mass of SPS being switched.

All membranes were cut into 4” x 2” rectangles. Each membrane type was placed into separate glass jars. Enough SPS was added to each jar to ensure complete immersion of all membranes. The jars were sealed and placed in the fume hood for storage. Membranes were exposed for 7, 15, 21, and 30 days. After the specified length of time was reached, the jar was drained of SPS, rinsed with deionized water, refilled with deionized water, and the membranes were stored in the jars for at least three days. Water was changed inside the jar daily. By rinsing the membranes in water, solvent is allowed to diffuse out of the polymer. This reverses the effects of the inevitable swelling which occurs and the membrane is effectively de-swelled.

2.3 Reverse Osmosis Characterization of exposed membranes

Exposed and rinsed membranes were next characterized using a bench-scale cross-flow RO testing system. The set-up for the system is as shown in Figure 8.

Membranes were placed in three cells with the active layer facing the feed solution. Trials were run at 20 °C, with an applied pressure of 225 psi and flow rate...
of 2 liter/min. Before beginning trials, 300 mL of pure water was allowed to permeate the membranes to further rinse them of SPS. The RO system was then flushed with clean water and trials began.

The system was allowed to equilibrate with 9 L of deionized water for 30 minutes. Pure water permeability was measured first. Trials were timed and mass of permeate was recorded to generate flux data. Water permeability, $A$, was then calculated using equation (2). 1 L of 20000 ppm NaCl was then added to the system to make a 2000 ppm solution, and allowed to equilibrate for 30 minutes. Conductivity of the bulk solution was measured using a conductivity probe. Trials were then timed and mass of permeate was recorded. Conductivity of permeate was recorded to give values for $C_p$. Final conductivity of the bulk solution was then recorded and averaged with the initial value and used as $C_f$. Parameters $R$ and $B$ were then able to be calculated using equations (4) and (5).

This testing procedure was repeated for each membrane at each exposure length. Each data point was run in duplicate.

3 Results and Discussion

Water permeability coefficient ($A$), solute permeability coefficient ($B$) and salt rejection ($R$) were measured using the RO testing procedure. We are interested in observing any changes in these performance parameters.

Modification of some SW30HR membranes were made and added to the data set. The polyester support layer was removed and stored leaving only the polyamide and polysulfone substrate for exposure. When the membrane was loaded for testing, the polyester backing was reincorporated for support. By removing the support it was hoped the membrane would better simulate an FO membrane which have much thinner support layers. It was speculated that the polyester layer could have been hindering amine diffusion into the polysulfone structure which would cause inaccurate reflection of any degradation. Results of RO testing will be used to verify whether performance is the same as the non-peeled SW30HR membrane. It will also help to confirm the behavior of the polyamide polymer in the presence of SPS.

3.1 $A$, $B$, $R$ Measurements

Plot 1 shows how water permeability coefficient ($A$) changed as a function of exposure time. Generally speaking, it did not significantly change for any membranes. Even if there is an increase in permeability, this is not necessarily a bad thing provided rejection and solute permeability does not suffer.
Plot 1: Water permeability coefficient (A) as a function of exposure time.

Plot 2: Solute permeability coefficient (B) as a function of SPS exposure time.
Plot 2 and Plot 3 prove that there is no significant change in solute permeability or salt rejection within error.

The peeled SW30HR membrane had similar performance to the non-peeled membrane. This means the polyester layer did not have any effect on the results. It also isolated the polyamide and polysulfone, showing that they are solvent tolerant.

The HTI-TFC showed the most variance between data points as illustrated by the large error bars. It was designed for use in FO which presents problems when using it in an RO application. Information about the membrane is proprietary yet one can speculate that it has a thinner polyamide layer and lower cross-link density. The low crosslinking density leads to lower salt rejection when there is a high pressure feed. This will not be an issue when used in FO which operates without an applied pressure. Other causes for this variance is membrane swelling. The membrane swells during SPS exposure, then de-swells during the rinsing process. The swelling and de-swelling process may induce microscopic tears causing large deviations in performance.

4 Conclusion
The RO testing conducted was able to show that the chosen TFC membranes are solvent tolerant. HTI-TFC is an FO membrane not designed for RO and had varying behavior likely for this reason. The use of RO membranes made of the same material proved the feasibility of using polyamide TFC membranes for forward osmosis applications.
5 Future Work

Because we now know that polyamide TFC membranes are compatible with SPS, we can begin to implement them for use with forward osmosis. Because the SPS is a solvent, it will dissolve many materials used to build a typical FO system such as PVC, and other materials containing plasticizers. To solve this problem, a solvent tolerant FO system, composed mostly of stainless steel, has been constructed and testing will begin soon to obtain flux measurements. Figure 9 shows the configuration of the FO system.

A brine solution and an amine solution are circulated using pumps and temperature controlled using heat exchangers. They pass through an FO cell where water is driven into the SPS draw solution. A scale measures the change in mass of brine and records it on a computer in order to calculate flux continuously.

A column which can switch the SPS according to the reaction in Figure 3 is incorporated into the system as diagramed in Figure 10. SPS is pumped into the column where it falls through packing material which enhances mass transfer between inlet gas entering from the bottom. A gas bypass is used when turning the gas off to prevent any SPS from backing up into the gas line. Excess gas exiting the top carries some SPS. The forward switching reaction is exothermic and as the gas cools on its way out of the column, some of the SPS is condensed for recovery and collected in a glass vessel.

The entire system operates either in switching mode or FO mode by turning a 3 way valve.

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References


