EFFECT OF SCALE DEPOSITION ON SURFACE TENSION OF SEAWATER AND MEMBRANE DISTILLATION

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Abstract

High liquid entry pressure (LEP) is one of the desired characteristics of a membrane distillation (MD) membrane. Maintaining LEP above operating feed pressure conditions is critical to prevent permeate quality worsening by saline feed liquid passage through the membrane. Air gap membrane distillation experiments under controlled salinity and temperature operating conditions indicate that in addition to flux decline, inorganic scaling can also lead to feed breakthrough and permeate salinity increase in some cases. The relationship between calcium sulfate and carbonate scaling and breakthrough was further illustrated by comparing the permeate quality obtained using clean and fouled membrane with seawater brine of $S = 120$ g/kg as feed at $t = 70$ °C. While contact angle changes and pore size variation have been considered to explain salt passage and LEP decrease, the effect of surface tension of the feed liquid under MD operating conditions has not been investigated. In a previous work, the authors measured reference data and created correlations for surface tension of seawater for $1 \leq t \leq 92$ °C and salinities $0 \leq S \leq 131$ g/kg. In the present study, new measurements investigating the effect of scaling on the surface tension of seawater are presented. Bulk precipitation was observed in seawater solutions for $t > 50$ °C. Membrane distillation operating conditions were simulated in the surface tension measurements where the test-beaker was reused between experiments after rinsing, which left behind a thin layer of scalant on the glass surface. Repeatable results under these conditions show marked decrease in surface tension (up to 30% at $S = 120$ g/kg) from standard correlations. This reduction in surface tension can cause LEP to reduce and increase salt passage in MD systems at $t > 50$ °C, as has been reported in the literature. The role of surface tension changes on MD separation effectiveness is recognized.
I. INTRODUCTION

Membrane distillation (MD) is a thermal desalination technology that has been actively developed over recent years, especially for renewable energy and waste-heat applications. Water is volatile, whereas dissolved salts and other impurities are not, and therefore water evaporates selectively out of a warm feed solution as pure vapor. The technology relies upon a hydrophobic membrane to establish menisci of hot saline water along its pores creating the surface area for evaporation. Vapor therefore has to only diffuse across the thickness of the MD membrane enabling compact scalable separation.

Scaling and fouling are concerns in MD, as in other membrane desalination technologies. Precipitation and growth of inorganic salt crystals leads to a reduction in water production by reducing the pore sizes or reducing the effective membrane area. In addition to flux decline, permeate water quality decline is also observed in some practical systems. Experimental investigation of the air gap MD (AGMD) process under supersaturated feed conditions over multiple days shows that while flux decline is common, liquid breakthrough and permeate quality decline also follow in some cases. Since MD relies on phase change for separation, under normal operating conditions near complete rejection of all salts and impurities is achieved. As a result, permeate conductivity is often lower than 10 μS/cm. Saline liquid breakthrough would manifest itself as an increase in the conductivity of the permeate stream.

Critical to MD process performance is the ability of the membrane to prevent liquid water from passing through. The minimum feed pressure required to overcome an MD membrane’s ability to resist liquid passage through the membrane pores is called the Liquid Entry Pressure (LEP). LEP is a function of the membrane hydrophobicity, feed liquid surface tension and the size of pore. LEP can also be defined locally at different regions of the membrane with the overall LEP being the least among these local values. Using an idealized model of the MD membrane consisting of circular pores, the LEP of the membrane can be written in terms of the liquid-vapor surface tension, the contact angle between the membrane and the liquid, and the membrane pore diameter as:

\[
LEP = \frac{-4B_g \gamma \cos \theta}{D_{\text{max}}}
\]

where \(B_g\) is a geometric factor for pores (\(B_g = 1\) for cylindrical pores), \(\gamma\) is the solution’s surface tension, \(\theta\) is the contact angle between the membrane and solution (typically \(\theta \geq \pi/2\)), and \(D_{\text{max}}\) is the membrane’s maximum pore size.

The decrease in LEP leading to breakthrough has been related to changes in contact angle \(\theta\) and pore structure resulting from scaling, whereas the effect of surface tension variation during operation has not been investigated.

Nayar et al. [1] recently reported reference data and a reference correlation for the surface tension of seawater as a function of temperature \(t\) and salinity \(S\) for temperatures \(1 \leq t \leq 92 \, ^{\circ}\text{C}\) and salinities \(0 \leq S \leq 131 \, \text{g/kg}\). To obtain the reference data, experiments were conducted on ASTM D1141 standard substitute seawater (or ASTM seawater) [2] using the Wilhelmy plate method. The reference correlation was used as a baseline for reference. In this work, we reported our experimental investigation into how precipitation and scale formation can affect the surface tension of ASTM seawater at elevated temperatures \((t > 50^\circ\text{C})\). While Nayar et al. generated reference data under very strict experimental conditions, here we present results obtained in operating conditions, i.e. with potential scale formation
and precipitation issues, similar to those seen in real-life MD installations. Surface tension experiments on ASTM seawater were also conducted in the range of temperatures and salinities relevant to seawater MD. The results obtained are expected to contribute to a better understanding of observed salt passage and LEP in MD.

II. MEMBRANE DISTILLATION SCALING AND LEP

A bench-top air gap MD (AGMD) apparatus was used to test fouling in membrane distillation at well-defined temperature, flow rate, and salinity conditions. The apparatus has been previously described and validated with numerical modeling, by Warsinger et al. [3]. Changes in permeate production rate were measured with a mass balance (accuracy of 0.1 g) while salt passage was detected by measuring permeate salinity using a conductivity meter (accuracy of 1%). Figure 1 shows a schematic diagram of the MD apparatus. Permeate water was periodically replenished into the feed tank to maintain the feed salinity at a fixed value during operation.

Figure 1. Membrane distillation system diagram. Hot saline feed and a cooling loop passed through an MD flat sheet module. Salinity, pressure, temperature, and mass flow rate measurements are taken at various locations within the system. Diagram modified from Ref. [3]

Figure 2 shows data from an experiment under scaling conditions. The feed solution was prepared by mixing 30.6 mmol/L of calcium chloride and sodium sulfate to generate a feed solution supersaturated with calcium sulfate. Calcium sulfate, like calcium carbonate, shows inverse solubility behavior, having lower solubility at higher temperatures and is therefore a common scalant in thermal desalination systems such as MD. Supersaturation is measured as a supersaturation index ($SI$), defined as the log of the ion activity product divided by $K_{sp}$. The $SI$ at the membrane interface on the feed side was calculated to be $SI = 0.4$, making it thermodynamically feasible for scale initiation and growth close to the
membrane. The feed bulk inlet temperature was maintained at \( t = 70 \, ^\circ\text{C} \) and the cold side at \( t = 20 \, ^\circ\text{C} \) using feedback controllers. The flux is evaluated by measuring the amount of permeate produced over time using a mass scale.

Figure 2(a) shows that the permeate flux declines over time, reducing by about 9% in 20 hours, indicating fouling and a decrease in effective membrane area. Figure 2(b) shows that the permeate quality starts declining, with conductivity increasing to above 300 \( \mu \text{S/cm} \) between time = 20-40 hours. Correspondingly, at this time, an increase in flux is observed, associated with salt water crossing the membrane at some regions locally, in addition to the pure water production by evaporation.

![Figure 2. Results from AGMD fouling test with supersaturated CaSO\(_4\) solution. Permeate conductivity increase observed following flux increase](image)

Experiments were carried out on the module with seawater brine at \( S = 120 \, \text{g/kg} \) and \( t = 70 \, ^\circ\text{C} \) to investigate the effect of fouling on salt rejection compared to a clean membrane. Figure 3(a) shows photographs of the clean (unfouled) and fouled membranes used in this study. The fouled membrane was prepared by adding a mixture of calcium chloride, sodium sulfate and sodium carbonate solutions on the membrane and allowing the solution to dry out, leaving behind a cake of calcium sulfate, calcium carbonate, sodium chloride and other salts. Similar scaling is likely to occur in solar MD plants under intermittent operation when the system is allowed to dry out overnight [4].

Figure 3(b) shows the permeate conductivity measured in both cases. While the clean membrane produced extremely pure water in spite of the high feed salinity, the fouled membrane allowed a small fraction of the part of the feed to pass through immediately, indicating a relationship between calcium sulfate carbonate fouling and reduced salt rejection.
Figure 3. Comparison of salt rejection by unfouled membrane and membrane using \( S = 120 \text{ g/kg} \) seawater brine as feed at \( t = 70 \degree \text{C} \) with \( \text{CaSO}_4 \), \( \text{CaCO}_3 \) and \( \text{NaCl} \) cake deposits

III. SURFACE TENSION AND SCALE FORMATION

3.1 Methodology

A detailed description of the methods used for measuring surface tension including the uncertainty analysis procedure is given in a previous publication by Nayar et al. [1] and in the master’s thesis work of the first author [5]. Briefly, the surface tension was measured using a DCAT11 tensiometer implementing the Wilhelmy plate method to within an uncertainty of 0.18 mN/m across a temperature range of \( 1 \leq t \leq 92 \degree \text{C} \). The test solution sample was taken in a borosilicate glass beaker. The temperature of the sample was controlled with the help of a Julabo F12-ED refrigerated and heating circulator. To reduce the loss of solvent due to evaporation and to reduce risks of environmental contamination, an aluminum lid for the beaker was designed and fabricated. The lid was heated using a strip heater. The temperature of the lid was kept to within 1-4 \degree \text{C} of the temperature of the test solution with the help of a separate Proportional-Integral-Derivative (PID) controller. A Fluke 5611T Teflon thermistor probe with accuracy 0.01 K was used to measure temperature of the sample. The test sample was stirred and the bulk solution temperature was measured to an uncertainty of 0.03 K. Seawater solutions of salinities \( S = (20.01, 39.99, 80.20 \text{ and } 120.01) \text{ g/kg} \) were prepared by either weigh-evaporating or by diluting solutions of ASTM D1141 standard seawater \( (S = 35.18 \text{ g/kg}) \). Overall, the uncertainty in salinity measurement varied from 0.09 g/kg to 0.87 g/kg. A schematic diagram of the experimental setup is shown in Fig. 4.
Before each surface tension experiment, the test beaker was cleaned by rinsing three times with Milli-Q deionized water and once with ACS reagent grade water, after which the beaker was dried in an oven. Clean task wipes (known commercially as Kimwipes) were used to absorb any remaining water droplets. The re-use of test beakers after rinsing and cleaning with water approximates maintenance regimes in a typical MD installation. MD membranes would be rinsed with water and re-used. It must be noted that the cleaning protocol used in this work was different from that used by Nayar et al. [1] to generate reference data. While Nayar et al. had used new test beakers for each surface tension experiment, in this work, beakers are re-used after cleaning. The difference in cleaning protocols is important as we observed in our experiments that a fine layer of scale, which wasn’t completely removable by simple rinsing with water, was typically left behind on the test beaker after a few hours of testing at $t > 50^\circ$C. The accumulation of this fine layer of scale with time over several experiments led to seawater surface tension measurements that are different from those of Nayar et al. for $t > 50^\circ$C. While the data of Nayar et al. are clearly reference values for seawater measured with high accuracy and control, values reported in this work highlight the effect of scale formation and potential adsorption of contaminants on the surface tension of seawater. To verify that the cleaning procedure used in this work does not have any inherent problems and to validate the procedure, surface tension experiments were also conducted on ACS water and aqueous sodium chloride solution.

![Figure 4. Schematic diagram of tensiometer](image-url)
Precipitation of sparingly soluble salts at $t > 50 ^\circ C$

Precipitation of sparingly soluble constituent salts of seawater was observed in seawater surface tension experiments when the test sample was heated to $t > 50 ^\circ C$. The precipitation of salts caused a change in appearance with test solutions gradually becoming milky white at temperatures greater than 50 ºC. This is shown in Fig. 5. However, precipitation by itself did not affect the accuracy or repeatability of surface tension measurements. This is evident from the reference data and uncertainties reported by Nayar et al., where precipitation of salts was allowed to occur, but clean new beakers were used for each experiment to prevent scale formation and buildup. Not only were the seawater reference measurements of Nayar et al. repeatable and accurate, they also matched Dutcher’s correlation for aqueous sodium chloride surface tension $[6]$ to within 1.2%. This is expected due to the high proportion of aqueous sodium chloride in seawater. The comparison is depicted in Fig. 6 with the markers representing data from Nayar et al., the dashed line representing surface tension as calculated from Dutcher’s correlation and the shaded line representing the reported deviation in Dutcher’s correlation.

Figure 5. Photograph highlighting the change in appearance of 35 g/kg seawater due to precipitation of sparingly soluble salts at $t > 50 ^\circ C$ which happened over 4 hours of experimentation at 70 ºC and 80 ºC
3.3 Effect of scale formation on test beaker on surface tension

While the precipitation of sparingly soluble salts did not affect the accuracy of surface tension measurements, scale formation on the test beaker that occurred over several hours of testing at high temperatures \( t > 50^\circ C \) coupled with the reuse of scaled test beakers decreased the measured value of seawater surface tension. This is depicted in Fig. 7. The markers refer to data while the dashed lines refer to the surface tension of seawater calculated from the reference correlation of Nayar et al. given by:

\[
\gamma_{sw} = \gamma_w + 3.766 \times 10^{-4} S + 2.347 \times 10^{-6} S t
\]  

(2)

where \( \gamma_{sw} \) is seawater surface tension in mN/m, \( S \) is reference salinity in g/kg, \( t \) is temperature in Celsius and \( \gamma_w \) is the pure water surface tension in mN/m as calculated from the IAPWS correlation [7]. The error bars shown in the figure correspond to the expanded uncertainty in the surface tension measurement which varied from 0.19 to 1.97 mN/m.
Figure 7. Measured surface tension of ASTM seawater decreasing below the surface tension of pure water after scale formation on the test beaker for \( t > 50^\circ C \); seawater surface tension from reference correlation of Nayar et al. given for comparison

Seawater surface tension decreased drastically for \( t > 50^\circ C \) when using a scaled test beaker; with the measured surface tension being lower than that of pure water in several cases. The largest reduction seen was 30% at \( S = 125 \text{ g/kg} \) and \( t = 90^\circ C \). For temperatures, \( t < 50^\circ C \), surface tension in general did not decrease, suggesting that salt solubility limits might play a role in decreasing surface tension at elevated temperatures. The exact mechanism for the decrease in surface tension at \( t > 50^\circ C \) could not be rigorously evaluated, but it is hypothesized that surface active material in the lab environment was adsorbed by the fine scale layer on the beaker and subsequently released into the test sample at elevated temperatures.

3.4 Comparison with literature LEP measurements

Guillen-Burrieza et al. [4] had analyzed scaled membranes from MD pilot plants after 2-3 years of operation and characterized them in contrast to unused membranes. Several cleaning protocols and their efficacies were also investigated. LEP measurement results are reproduced below in Fig. 8. For \( t > 50^\circ C \), a lower LEP is observed with the fouled membrane as compared to the unused membrane. The difference becomes significant for \( t = 60^\circ C \), similar to the trend observed in Fig. 7. This strong temperature dependence of the LEP of the fouled membrane suggests that the observed decrease in surface tension at high temperatures plays an important role in reducing LEP. Surface tension changes of seawater should therefore be considered in future design and analysis of MD membranes and process.
IV. CONCLUSIONS

Experiments on salt passage in air gap membrane distillation showed decreased salt rejection associated with scaling on the membrane. Surface tension measurements showed that scale deposited by precipitation of sparingly soluble salts in seawater under simulated real-life MD operating conditions, reduced the surface tension at $t > 50^\circ\text{C}$ and $S > 35 \text{ g/kg}$ by up to 30%. This phenomenon is expected to contribute to the reduction in liquid entry pressure (LEP) of membrane distillation membranes at elevated temperature under fouled conditions. Data from literature on MD LEP measurements also shows similar temperature dependent trends that correlate well with measured surface tension variations. Surface tension changes under MD operating conditions should therefore be considered in conjunction with contact angle and pore-size effects to better describe this critical characteristic of MD membranes.

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Figure 8. LEP measurements with 35 g/kg NaCl solution: comparison between unused and fouled membranes (reproduced from [4])
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VI. REFERENCES


