Model thin film composite membranes for forward osmosis: Demonstrating the inaccuracy of existing structural parameter models

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A B S T R A C T

Structural parameter, or $S$, is a widely used metric for assessing a membrane’s suitability for use in osmotic processes. Currently, $S$ is only calculated by an indirect approach using models derived from the governing flux equation. Our prior work has shown that this method is fraught with inaccuracy and that the true, or intrinsic, $S$ value can differ substantially from the effective $S$ value determined by fitted parameter methods. In this work, we prove that hypothesis definitively by using a membrane with a structural parameter that is known a-priori. We synthesized a thin film composite membrane using a well-characterized porous support membrane. The material we chose as the support is a polycarbonate track-etched membrane, which has an easy-to-characterize thickness, porosity, and tortuosity. These membranes have an intrinsic structural parameter of 133 μm but an effective structural parameter that ranged widely from 159 μm to 1950 μm when quantified using conventional methods. This finding should cause concern regarding the validity of existing mass transfer models. New approaches are necessary to fairly compare new membranes designed for osmotic processes.

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1. Introduction

Forward osmosis (FO) is a membrane-based technology platform with several applications in varied fields such as desalination [1–5], power production (pressure-retarded osmosis, PRO), concentration [6–8] and dewatering [9,10] and many others. FO relies on water being driven across a selective membrane as a result of osmotic pressure gradients between two solutions, the saline feed and a draw solution with a relatively higher solute concentration. While work in FO has caused a recent flurry of research in systems [11,12] and draw solution design [11–13] much of the recent published work has been centered on membrane design. Many of these efforts have been inspired by the thin film composite (TFC) structure widely used in reverse osmosis (RO). TFC FO membrane design departs from RO TFC membranes, however, by employing a support that is designed for high porosity, low tortuosity, and minimal thickness. These features, while unimportant for RO, minimize the structural parameter, which is a metric that is used to ascertain a membrane’s propensity to cause internal concentration polarization (ICP). $S$ can be described as the average diffusive path length through the support structure, and is described by the equation

$$S_{\text{eff}} = \frac{\tau \epsilon}{\varepsilon}$$

where $t$ is the thickness, $\tau$ is the tortuosity, and $\epsilon$ is the porosity of the membrane support structure. $S$ is widely used by both academic and industry researchers as an assessment of membrane structural characteristics for osmotic processes. To determine the value of $S$, we might consider calculating the individual values of $t$, $\tau$ and $\epsilon$. While this may sound trivial, measuring porosity and tortuosity, especially of soft materials, is a challenge. We describe these techniques and challenges in our recent publications [14,15]. These challenges have led most of the research community to adopt a fitted parameter mass transfer model to determine $S$ from empirical data. The model for when the selective layer faces the draw solution (the PRO mode) is [16]

$$S_{\text{eff}} = \frac{D}{J_w} \ln \frac{B-J_w+A \pi_{D,m}}{B+A \pi_{f,b}}$$

When the selective layer faces the feed solution (the FO mode) the model is

$$S_{\text{eff}} = \frac{D}{J_w} \ln \frac{B+A \pi_{D,b}}{B+J_w+A \pi_{f,m}}$$

In these two models, $S_{\text{eff}}$ is the “effective” or fitted structural parameter, $D$ is the solute diffusivity, $J_w$ is the average water flux, $A$ is the membrane permeance, $B$ is the membrane salt permeability.
coefficient, \( \pi_0 \) is the osmotic pressure of the draw solution, and \( \pi_c \) is the osmotic pressure of the feed solution. Subscripts \( m \) and \( b \) indicate values at the membrane surface and in the bulk solution respectively. The problems associated with using these models have been examined previously by a number of research groups. In one such study where Cath et al. [17] were looking to establish a method to standardize FO testing, the authors reported results obtained by seven research groups in testing two types of membranes from the same batch and under the same experimental conditions. The average \( S \) value obtained by the different lab groups was around 535 μm with a standard deviation of about 163 μm which was found to be a non-negligible variation in the context of the study. Further, Wong et al. [18] reported that \( S \) of the HTI-CTA membrane varied with type, concentration, and even temperature of the draw and feed solutions. These changes had been attributed to possible swelling and dewelling behavior of the cellulose tri-acetate polymer which has a tendency to absorb water [19]. Furthermore, another fundamental problem with these models is how the values for \( A \) and \( B \) are determined. In most of the work, the \( A \) and \( B \) parameters are obtained from RO tests. This method is questionable since \( A \) and \( B \) are likely different under pressure in RO than they are in FO. Furthermore, the concentration of the solute in contact with the membrane selective layer is much lower in RO tests than that in FO tests. The discrepancy between \( A \) and \( B \) values in FO being different from that in RO has been pointed out by Tiraferri et al. [20]. That study showed that there were variations in the \( A \) and \( B \) values calculated for the four membranes studied (2 TFC FO, 1 asymmetric FO and 1 TFC RO) using the two approaches (RO versus FO) and the variations in \( B \) were found to be quite significant for the 2 TFC FO membranes.

To better understand how these models may or may not be accurate, we consider membranes with a structural parameter that is known \textit{apriori}. We do this by selecting a support structure that has a pore structure consisting of straight, cylindrical pores, (\( r = 1 \)) and a well-defined thickness and porosity. Using a model structure was preferred since some of the structural characteristics, such as tortuosity, are difficult to characterize accurately as discussed by the authors in their previous publication [15]. The membrane must also be self-wetting (i.e. hydrophilic) so that “incomplete” wetting during osmotic flux measurements does not artificially exaggerate the structural parameter value [14]. We identified track-etched (TE) membranes as having these necessary characteristics. Building a selective layer on top of these membranes would create a TFC membrane with a well-defined structural parameter. Testing under RO and FO conditions would allow us to compare this intrinsic value to the effective \( S \) value calculated by conventional means. The comparison identified that the validity of existing models are questionable and that new characterization approaches for osmotic membranes are necessary.

2. Materials and methods

2.1. Materials

2.1.1. Choice of support layer

The TE support needed to have a pore size rating capable of supporting the polyamide thin film without causing conformal coating during its formation as well as yield reasonable water permeation rates. A 0.2 μm pore size TE membrane (Maine Manufacturing) made of hydrophilized polycarbonate was identified as a viable candidate and was used as the support for TFC membranes.

2.1.2. Reagents and membranes

Aqueous diamine monomer \( m \)-phenylene diamine (MPD, > 99%) and organic acid chloride monomer 1,3,5-benzenetricarbonyl trichloride (TMC, 98%) were purchased from Sigma-Aldrich. Deionized (DI) water obtained from an ultrapure water purification system (Integral 10, Millipore) was used as the solvent for MPD. Hexane (Fisher Scientific) was used as the solvent for TMC. Sodium chloride, NaCl (Fisher Scientific) was used as the solute for RO and FO testing. Commercially-available asymmetric cellulose triacetate (CTA) FO membranes, provided by Hydration Technology Innovations (HTI, Albany, OR) were tested as a control. These membranes are designated as HTI-CTA throughout this article.

2.2. Methods

2.2.1. Interfacial polymerization

For in-situ formation of the polyamide thin film 1% (w/v) MPD and 0.15% (w/v) TMC solutions were formed by dissolving the monomers in their respective solvents and stirring for at least 3 h prior to using. First, the TE support was taped onto a glass plate and then immersed into the MPD solution for 120 s. Excess MPD was removed from the surface using a rubber roller before placing in the TMC solution for 60 s. The resulting composite film was immediately placed in an air-circulation oven, kept at 80 °C for 4 min to dry-cure. Any excess reagents were washed off in two successive DI water baths for 5 min each. The TFC membrane, designated as TE-CTA hereafter, was then stored under DI water at 4 °C until further use.

2.2.2. Membrane characterization

Surface morphology and cross-sections of the TFC membrane were obtained using a cold cathode field-emission scanning electron microscope (FE-SEM) JSM-6335F (FEI). A thin layer of platinum was sputter-coated onto the samples prior to imaging to obtain good contrast and avoid charge accumulation. The cross-sections were obtained by freeze-fracturing the sample in liquid nitrogen. Surface images of the TE membrane were also obtained to determine the support’s porosity by performing image analysis (ImageJ, National Institutes of Health).

2.2.3. Determination of pure water permeance, solute permeability coefficient, and solute rejection from cross-flow RO

Pure water permeance, \( A \), of the TE-TFC membrane was obtained by testing in a cross-flow RO system. The membrane was tested under four trans-membrane hydraulic pressures ranging from 6.89–17.24 bar (100–250 psi) at a cross-flow velocity of 0.26 m/s at 20 °C. Salt permeability coefficient, \( B \) and intrinsic salt rejection, \( R_{\text{int}} \) were determined using a 2000 ppm NaCl feed at 15.5 and 27.6 bar. Feed and permeate conductivity measurements were made using a conductivity probe in these tests. \( A \), \( B \) and \( R_{\text{int}} \) were calculated using formulae available elsewhere [21]. The HTI-CTA was tested as a control. Triplicate tests were performed for both membranes.

2.2.4. Evaluation of osmotic water flux and reverse salt flux

Osmotic water fluxes and reverse salt fluxes of the TE-TFC membrane were determined by testing in a custom-built cross-flow FO system. Details of the system set-up are available elsewhere [22]. Tests were performed by orienting the membrane in both FO (selective layer facing the feed) and pressure-retarded osmosis, PRO (selective layer facing the draw) modes. The membranes were tested at 20 °C at a cross-flow velocity of 0.26 m/s at 0 trans-membrane pressure (3 psi hydraulic pressure on both sides). Draw solution concentrations of 0.5, 1.0 and 1.5 M NaCl were used while DI water was used as the feed for all tests. The conductivity of the feed solution was monitored using a conductivity probe to measure the reverse salt flux. The HTI-CTA membrane was tested as a control. Triplicate tests were performed for both membranes. The external concentration polarization modulus on the membrane selective layer side was calculated using correlations,
available in literature [21], between the mass transfer coefficient, $k$ and the Sherwood number for a rectangular channel.

2.2.5. Calculation of structural parameters

The intrinsic structural parameter, $S_{intrinsic}$ of the TE-TFC membrane was calculated using the porosity value obtained from SEM image analysis. Tortuosity was verified to be unity from cross-section SEM images and the TE support thickness stated by the manufacturer was verified using a micrometer. The effective structural parameter of the membrane was calculated using the governing equations for water flux in PRO (Eq. (2)) and FO modes (Eq. (3)).

3. Results and discussion

3.1. Characterization of TE and TE-TFC membranes

Fig. 1a shows the pores in the track-etched membrane. The average porosity obtained from analysis of multiple images was 13 ± 2%. We assume that each of the pores is a straight through pore [21] (see the cross-section of the support in Fig. 1b), meaning that the surface porosity is equal to the bulk porosity. These straight pores also imply that the tortuosity equals one. Using the known thickness of the TE membrane (20 µm), the intrinsic structural parameter was calculated to be 133 µm. This assumes that the polyamide layer that forms on the TE membrane does not form inside the pores.

3.2. Pure water permeance, solute permeability coefficient, and solute rejection from cross-flow reverse osmosis

Fig. 1c shows that a polyamide layer, having a rough morphology, was formed after interfacial polymerization on the support. The selective layer characteristics, for both the TE-TFC and the control HTI-CTA, determined from cross-flow reverse osmosis (RO) tests, are shown in Table 1. The salt permeability coefficient, $B$ of the TE-TFC exhibited broader standard deviations than the HTI-CTA, which is common for hand-made TFC membranes. The TE-TFC exhibited reasonable salt rejections, similar to that of the HTI-CTA, and pressure tolerance indicating that the polyamide layer maintained its integrity during the test.

3.3. Osmotic flux performance of TE-TFC membranes

Fig. 2 shows the osmotic water flux performance of the TE-TFC at draw solution concentrations of 0.5, 1.0 and 1.5 M NaCl with DI water feed. Fluxes of the HTI-CTA are also shown. The water flux increased with draw concentration as expected. The FO and PRO mode fluxes of the TE-TFC matched well for all three draw concentrations indicating that the membrane performance was perhaps independent of its orientation. This is a curious result, since usually PRO mode fluxes of EO membranes are almost always greater than their corresponding FO mode counterparts, especially when using a DI water feed, as a result of more severe ICP in the FO mode compared to that in the PRO mode.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Water permeance, $A$ (l m⁻¹ h⁻¹ bar⁻¹)</th>
<th>Salt permeability coefficient, $B$ (l m⁻¹ h⁻¹)</th>
<th>Intrinsic NaCl rejection, $R_{intrinsic}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TE-TFC</td>
<td>0.417 ± 0.012</td>
<td>0.754 ± 0.366</td>
<td>15.5 bar: 94.89 ± 2.77</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>27.6 bar: 88.63 ± 4.51</td>
</tr>
<tr>
<td>HTI-CTA</td>
<td>0.616 ± 0.026</td>
<td>0.699 ± 0.199</td>
<td>15.5 bar: 94.11 ± 2.09</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>27.6 bar: 95.34 ± 1.29</td>
</tr>
</tbody>
</table>

Fig. 1. SEM image of (a, b) top and cross-section of 0.2 µm track-etched membrane (TEM) and (c) TE-TFC membrane formed on the TEM. Inset in 1c depicts a larger field-of-view showing the relatively homogeneous morphology of the polyamide layer. Images 1a and b were used to calculate porosity and ascertain tortuosity respectively. Image 1b can also be used to ascertain thickness.
This typical behavior is seen here in the HTI-CTA performance. The reverse solute fluxes, shown in Fig. 3, show an expected similar trend, increasing with draw concentration for both membranes, with the PRO mode salt fluxes being larger than the corresponding FO mode ones for the HTI-CTA membrane due to the higher water fluxes. No clear differences were visible between the two modes for the TE-TFC membrane since the error bars for the FO mode were large which is common in a number of osmotic tests of hand-made membranes and when deionized water feeds are used. It is to be noted however that while the rather unconventional nature of the track-etched support is a likely reason behind the variability observed in the salt flux, this data is not used to make any significant conclusions nor are they used in the calculation of the $S_{\text{av}}$ values.

### 3.4. Structural parameters in FO and PRO modes

The $S$ values of both the TE-TFC and HTI-CTA membrane were calculated, using Eqs. (2) and (3), at the different draw concentrations and are tabulated in Table 2. In PRO mode the $S$ values for both membranes were found to vary significantly between the different coupons tested and with change in draw concentration as well. This is possibly due to the differences in $A$ and $B$ values of membranes in an RO versus an FO test [20]. In the PRO mode, both water and salt flux are relatively high implying a greater influence of $A$ and $B$ in the calculation of $S$. Variability or inaccuracy in the measurement of membrane selective layer properties would thus result in inaccuracy of the $S$ values calculated. The variations between the different membrane coupons at each draw concentration decreased for the TE-TFC membrane whereas for the HTI-CTA they continued to be rather large. In the case of the latter, it is possible that osmotic deswelling at high solute concentrations, leading to structural changes, could further exacerbate the effect of inaccurate $A$ and $B$ values.

In the FO mode, a similar decrease in $S$ with increase in draw concentration was observed with the overall change in the value being relatively smaller for the HTI-CTA compared to that of the TE-TFC. This is due to the $B$ value of the hand-made TE-TFC varying over a wider range than the HTI-CTA (Table 2). This variation in salt permeability of the TE-TFC membrane between different coupons, when incorporated in Eq. (3), is reflected as a change in $S$. Not surprisingly, the effective $S$ values of the TE-TFC membrane obtained at different testing conditions were generally far removed from the known $S_{\text{av}}$ value of 133 μm. These conditions are completely independent from the membrane structure itself, yet cause a non-negligible differences in structural parameter. This clearly necessitates the need for a change to the current approach of characterizing FO membranes’ structure in order to accurately identify and quantify the characteristics of membranes that hinder membrane performance.

### 4. Conclusions

This study proves that existing methods of calculating $S$ in asymmetric and TFC membranes are inaccurate. These methods, which include a number of fitted parameter models, fail to account for the numerous mass transfer resistances present across the membrane. The resulting inaccuracies in the calculation of $S$ may mislead membrane designers into overemphasizing the importance of $S$ when designing new membranes for FO. We should develop methods to account for these resistances and attribute only the structural resistances to the $S$ value. This is difficult, however, since such an analysis would require the use of empirical correlations that may or may not be appropriate for the system geometry or may require data which is estimated or unavailable (such as diffusivity) for individual solutes or mixtures of solutes. Another option is to measure the $S$ value directly using imaging and/or analytical tools. Many of these tools, however may only offer limited resolution or may have an inherent bias depending on their operating conditions. While a definitive solution to this problem is not offered as part of this study, researchers and membrane designers working in this area should be cognizant of the limitations of the existing methods.

### Acknowledgments

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**Table 2**

<table>
<thead>
<tr>
<th>Draw solution concentration, M</th>
<th>TE-TFC PRO</th>
<th>FO mode</th>
<th>HTI-CTA PRO</th>
<th>FO mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>1917 ± 508</td>
<td>621 ± 3</td>
<td>1077 ± 523</td>
<td>485 ± 131</td>
</tr>
<tr>
<td>1.0</td>
<td>1165 ± 127</td>
<td>480 ± 15</td>
<td>773 ± 364</td>
<td>445 ± 65</td>
</tr>
<tr>
<td>1.5</td>
<td>758 ± 114</td>
<td>219 ± 9</td>
<td>527 ± 377</td>
<td>398 ± 72</td>
</tr>
<tr>
<td>Average</td>
<td>1280 ± 588</td>
<td>440 ± 204</td>
<td>793 ± 275</td>
<td>443 ± 43</td>
</tr>
</tbody>
</table>

**Fig. 2.** Osmotic water fluxes of the TE-TFC membrane in PRO and FO membrane orientations. Data for a commercial FO membrane, the HTI-CTA is shown for comparison. Tests were performed at 20°C, 0.26 m/s cross-flow velocity with DI water feed at 0 transmembrane pressure. Three membrane coupons were used for all tests.

**Fig. 3.** Reverse salt fluxes of the TE-TFC membrane in PRO and FO membrane orientations. Data for a commercial FO membrane, the HTI-CTA is shown for comparison. Tests were performed at 20°C, 0.26 m/s cross-flow velocity with DI water feed at 0 transmembrane pressure. Three membrane coupons were analyzed for all tests.
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