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

Seetha S Manickam, Jeffrey R. McCutcheon\*

Department of Chemical &amp; Biomolecular Engineering, Center for Environmental Sciences and Engineering, University of Connecticut, Storrs, CT, USA

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## ABSTRACT

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  $133 \mu\text{m}$  but an effective structural parameter that ranged widely from  $159 \mu\text{m}$  to  $1950 \mu\text{m}$  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

$$S_{int} = \frac{t\tau}{\varepsilon} \quad (1)$$

where  $t$  is the thickness,  $\tau$  is the tortuosity, and  $\varepsilon$  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  $\varepsilon$ . 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]

$$S_{eff} = \frac{D}{J_w} \ln \frac{B - J_w + A\pi_{D,m}}{B + A\pi_{F,b}} \quad (2)$$

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

$$S_{eff} = \frac{D}{J_w} \ln \frac{B + A\pi_{D,b}}{B + J_w + A\pi_{F,m}} \quad (3)$$

In these two models,  $S_{eff}$  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

\* Correspondence to: University of Connecticut 191 Auditorium Rd, Unit 3222, Storrs, CT 06269-3222. Tel.: +1 860 486 4601; fax: +1 860 486 2959.

E-mail address: [jeff@engr.uconn.edu](mailto:jeff@engr.uconn.edu) (J.R. McCutcheon).

coefficient,  $\pi_D$  is the osmotic pressure of the draw solution, and  $\pi_F$  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  $\mu\text{m}$  with a standard deviation of about 163  $\mu\text{m}$  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 deswelling 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 *a priori*. We do this by selecting a support structure that has a pore structure consisting of straight, cylindrical pores, ( $\tau=1$ ) 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  $\mu\text{m}$  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-TFC 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,  $\%R_{int}$  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  $\%R_{int}$  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,

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