Contents lists available at ScienceDirect





Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Studying water and solute transport through desalination membranes via neutron radiography



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ARTICLE INFO

Keywords: Neutron radiography Forward osmosis Concentration polarization Wetting

ABSTRACT

Neutron radiography, a non-destructive imaging technique, is applied to study water and solute transport through desalination membranes. Specifically, we use neutron radiography to quantify lithium chloride draw solute concentrations across a thin-film composite membrane during forward osmosis permeation. This measurement provides direct visual confirmation of incomplete support layer wetting and reveals significant dilutive external concentration polarization of the draw solution outside of the membrane support layer. These transportlimiting phenomena have been hypothesized in previous work and are not accounted for in the standard thinfilm model of forward osmosis permeation, resulting in inaccurate estimations of membrane transport properties. Our work demonstrates neutron radiography as a powerful measurement tool for studying membrane transport and emphasizes the need for direct experimental measurements to refine the forward osmosis transport model.

1. Introduction

Polymeric thin-film composite membranes, which comprise a thin polyamide selective layer and a thick porous support layer, are the state-of-the-art technology for desalination applications such as reverse osmosis and forward osmosis because of their high water permeability and salt rejection characteristics [1]. Transport behavior for these thinfilm composite membranes is traditionally described by a solution-diffusion mechanism [2], where the driving force for permeation is hydraulic pressure in reverse osmosis and osmotic pressure in forward osmosis. Concentration polarization at the membrane surface may inhibit transport [3], and it is particularly detrimental to forward osmosis permeation, which experiences concentration polarization effects on both the selective layer and support layer sides of the membrane [4].

For forward osmosis, concentration polarization presents specific challenges for membrane design and transport modeling. Forward osmosis permeation from a low osmotic pressure feed solution, across a salt-rejecting membrane, into a high osmotic pressure draw solution is described by the standard film model [5]:

$$J_{w} = A \left(\frac{\pi_{D,b} \exp\left(-\frac{J_{w}S}{D}\right) - \pi_{F,b} \exp\left(\frac{J_{w}}{k_{F}}\right)}{1 + \frac{B}{J_{w}} \left(\exp\left(\frac{J_{w}}{k_{F}}\right) - \exp\left(-\frac{J_{w}S}{D}\right)\right)} \right)$$
(1)

where J_w is permeate flux; A, B, and S are membrane transport parameters described below; and D is the aqueous diffusion coefficient for the draw solute. Osmotic pressures of the bulk draw solution $(\pi_{D,b})$ and bulk feed solution $(\pi_{F,b})$ are assumed to be linearly related to the solute concentrations via the van't Hoff equation [5]. k_F is the mass transfer coefficient in the feed solution channel, which is estimated from a Sherwood correlation for laminar flow [4]. Concentration polarization boundary layer thickness, δ , may be calculated from the diffusion and mass transfer coefficients [6] using the relationship $\delta = \frac{D}{k}$.

The performance of the polyamide membrane selective layer is described by the water permeability coefficient (A, L m⁻² h⁻¹ bar⁻¹) and solute permeability coefficient (B, L m⁻² h⁻¹) [2]. Support layer resistance to transport is expressed as the membrane structural parameter (S, µm) [7]. The A, B, and S parameters are engineering transport properties of the membrane that are determined by fitting experimental measurements of permeate flux and salt rejection to the film model [5], the advantage of which is estimating transport properties from actual

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http://dx.doi.org/10.1016/j.memsci.2017.10.046

Received 19 May 2017; Received in revised form 10 October 2017; Accepted 23 October 2017 Available online 25 October 2017 0376-7388/ © 2017 Published by Elsevier B.V. membrane operating conditions [8]. These parameters provide a common set of criteria for comparing membrane performance.

The standard film model assumes boundary layers at the membrane selective layer and within the support layer that account for concentration polarization effects. External concentration polarization at the feed solution side of the polyamide selective layer is described by the external concentration polarization modulus, $ECP_F = \exp\left(\frac{J_W}{k_F}\right)$, a term that appears in both the numerator and denominator of Eq. (1) and that accounts for local concentration of solutes that are rejected by the selective layer and those that diffuse from the draw solution side, respectively [4,5,9]. Dilutive internal concentration polarization of the bulk draw solution within the porous support layer is described by the internal concentration polarization modulus, $ICP_D = \exp\left(\frac{-J_WS}{D}\right)$, which accounts for dilution due to the permeate flux (numerator of Eq. (1)) and the decrease in draw salt concentration at the membrane selective layer due to the reverse permeation of draw solute (denominator of Eq. (1)) [5,9,10]. Dilutive external concentration polarization (*ECP*_D) at the draw solution side of the membrane support layer [11] is assumed to be negligible, and dilutive ICP_D has been identified as the most significant factor reducing the driving force for forward osmosis permeation [4,6]. Improving support layer properties to reduce the structural parameter and associated ICP_D is critical to improving forward osmosis process performance [12,13].

The standard film model (Eq. (1)) is a relatively simple analytical description of forward osmosis transport and is widely implemented. While the model is effective at predicting permeate flux from experimental conditions, the membrane transport properties estimated from the model have been shown to be model-dependent and can change with experimental conditions [5,14]. Two specific challenges in forward osmosis transport modeling are incomplete wetting of the support layer and overestimation of the support layer structural parameter.

1.1. Incomplete support layer wetting

Porous polysulfone is a common support layer material in commercial desalination membranes. As polysulfone is a relatively hydrophobic material, there are concerns that polysulfone membrane supports do not fully wet during osmotically-driven desalination processes [15]. Incomplete wetting reduces the effective porosity for permeation and may exacerbate dilutive ICP_D in the support layer [15], which would also impact the membrane transport properties estimated from the standard film model.

Recent studies have indicated that increasing the hydrophilicity of polysulfone membrane supports can increase permeate fluxes in forward osmosis, which is attributed to an increase in wetted porosity in the support layer. Examples include coating commercial membrane supports with polydopamine [16] and poly(vinyl) alcohol [17] or blending sulfonated polymers into conventional polysulfone [18] and polyethersulfone [19] support layer materials. Concerns about incomplete support layer wetting and its detrimental impacts on forward osmosis performance are also reflected in standard testing protocols for osmotically-driven membrane processes, which specify membrane support layer wetting with isopropanol in an attempt to remove air bubbles [14].

1.2. Overestimation of support layer structural parameter

The standard film model for forward osmosis permeation assumes all transport resistance on the support side of the membrane occurs within the support layer, neglecting any dilutive ECP_D in the draw solution outside of the support. Support layer structural parameters are believed to be overestimated as a result [20]. For model membranes whose support layer thickness (t_s), porosity (ε), and pore tortuosity (τ) are known, the structural parameter *S* may be calculated from the support layer properties, rather than estimated from fitting experimental measurements [7]:

$$S = \frac{(thickness)(tortuosity)}{porosity} = \frac{t_s \tau}{\varepsilon}$$
(2)

Experimental determinations of the structural parameter for model membranes have consistently overestimated the *S* value compared to the calculated value from Eq. (2) under all experimental conditions [20]. Estimated *S* values for the same membrane tested under different conditions have also been shown to vary depending on the membrane orientation and draw solution concentration [20,21]. The differences between structural parameters estimated from the film model and those calculated from materials properties have been attributed to various factors including asymmetry in the support layer structure and the exclusion of some support layer properties from the structural parameter definition [8].

1.3. Need for direct measurements

To address challenges in forward osmosis transport modeling and improve estimates of the membrane structural parameter, expansions to the standard film model have been proposed [6], and numerical solutions using both finite element modeling [22] and computational fluid dynamics [23] have been undertaken. These efforts indicate the presence of dilutive ECP_D at the interface between the support layer and the draw solution. Importantly, both numerical simulations accurately predicted the experimentally measured forward osmosis permeate flux using a constant structural parameter, suggesting that support layer properties can be isolated from descriptions of other transport behavior. However, recent numerical modeling has also shown that support layer properties that are not included in the definition of the structural parameter (Eq. (2)), such as pore radius, may also influence forward osmosis transport behavior [24].

Additions or expansions to the standard film model improve permeate flux prediction, but the improvements may simply be a result of additional fitting variables. Direct measurements of water and solute transport in the membrane boundary layers during permeation are necessary to elucidate the relevant transport-limiting phenomena and to validate the most appropriate forward osmosis transport model. In practice, direct measurements, such as gravimetric determination of permeate flux or conductivity measurements to determine draw solute concentration, have been limited to bulk solution measurements because the boundary layers that develop near the membrane are inaccessible to these conventional measurement techniques. Direct measurements in the membrane boundary layers can improve membrane design by informing better modeling of membrane transport behavior and yielding more accurate estimates of membrane transport properties.

In an effort to provide direct measurements of water and solute transport, we apply neutron radiography, a non-destructive imaging technique, as a quantitative tool to study transport through desalination membranes. Specifically, we use this tool to investigate the wetting properties of thin-film composite membranes and the support layer structural parameter by directly observing draw solute concentrations across the membranes during forward osmosis permeation. We observed incomplete membrane support layer wetting and dilutive ECP_D behavior, which have been previously speculated but unconfirmed, and which are neglected in the standard film model.

2. Experimental

2.1. Thin-film composite membrane samples

Thin-film composite membranes for the neutron radiography experiments were fabricated with polyamide selective layers and commercial polysulfone ultrafiltration membranes (Sepro PS20) or tracketched polycarbonate membranes (Sterlitech Corporation) as support



Fig. 1. Thin-film composite membrane fabrication process using molecular layer-by-layer (mLbL) polyamide films. A) Silicon substrate is coated in release layer of 5% by mass poly (acrylic acid) (PAA) in deionized water. B) Solution of 1% by mass *m*-phenylenediamine (MPD) in toluene is deposited on the substrate, followed by rinsing with acetone. C) Solution of 1% by mass trimesoyl chloride (TMC) in toluene is deposited on the substrate, followed by rinsing with toluene. D) Deposited MPD and TMC monomers react to form a cross-linked polyamide film. Monomer solution depositions and rinses are repeated for 60 cycles. E) Adhesive layer of 2% by mass poly (*n*-butyl acrylate-*co*-acrylic acid) p(*n*BA-*c*-AA) in toluene with a monomer feed ratio of 0.05/0.95 (*n*BA/AA) is deposited on the polyamide film. F) Membrane support layer (polysulfone or polycarbonate) is adhered to the polyamide selective layer using fingertip pressure. G) The composite membrane is released from the substrate by dissolving the PAA release layer in deionized water.

layers [25]. The polyamide selective layer was formed using a spinassisted molecular layer-by-layer (mLbL) deposition technique [26] involving sequential deposition of 60 cycles of trimesoyl chloride (TMC, Sigma-Aldrich) monomer solution (1% by mass in toluene), toluene rinse, m-phenylenediamine (MPD, Sigma-Aldrich) monomer solution (1% by mass in toluene), and acetone rinse onto a silicon substrate that was coated with a release layer made of 5% by mass poly(acrylic acid) (PAA, $M_w > 200,000 \text{ g mol}^{-1}$, Polysciences, Inc.) in deionized water (18.1 M Ω cm, Barnstead Nanopure, Thermo Scientific). The polyamide film was then adhered to the membrane support layer using a 2% by mass solution of poly(n-butyl acrylate-co-acrylic acid) (p(nBA-c-AA)) (*n*BA, AA, Sigma-Aldrich) monomers in toluene at a monomer feed ratio of 0.05/0.95 (nBA/AA). Fingertip pressure was applied to adhere the selective layer to the support, and the resulting composite membrane was released from the silicon substrate by immersion in deionized water. The process for fabricating the thin-film composite membranes is shown in Fig. 1.

Thin-film composite polyamide membranes fabricated using the mLbL deposition process can mimic the salt rejection and permeate flux performance of membranes formed by traditional interfacial polymerization [27]. Using mLbL deposition rather than interfacial polymerization to create the polyamide selective layers was advantageous in that the surface roughness of the mLbL films is two orders of magnitude less than interfacially-polymerized membranes [28], which reduced the possibility of surface roughness blurring the neutron images. The interfacial polymerization process convolutes the support layer and polyamide selective layer properties. Thus, an additional advantage of mLbL deposition was the ability to fabricate composite membranes using different support materials while maintaining consistent polyamide selective layer properties.

Composite membranes with polysulfone supports were fabricated to mimic the most common materials of commercial desalination membranes and to investigate the wetting behavior of these hydrophobic supports. To experimentally investigate estimates of the support layer structural parameter from the standard film model, composite membranes were also fabricated from track-etched polycarbonate supports with known intrinsic material properties. For the track-etched polycarbonate membranes ($t_s = 6 \ \mu m, \ \tau = 1, \ e = 0.03$), the structural parameter calculated according to Eq. (2) is $S = 200 \ \mu m$.

The water permeability and solute permeability coefficients of the polyamide and polycarbonate composite membranes were determined from forward osmosis permeation tests of six different samples that were distinct from the samples used in the neutron radiography experiments. An established protocol was used to fit experimental data to the standard thin-film model [5], and the membrane structural parameter was fixed at $S = 200 \,\mu\text{m}$. The estimated (mean \pm standard deviation) water permeability coefficient A is $0.46 \pm 0.18 \,\text{Lm}^{-2} \,\text{h}^{-1}$ bar⁻¹, and the estimated solute permeability coefficient B is $0.04 \pm 0.02 \,\text{Lm}^{-2} \,\text{h}^{-1}$.

A similar mLbL deposition technique was previously used to fabricate 60-cycle polyamide composite membranes for a forward osmosis application [29]. The previously fabricated mLbL membranes had water permeability coefficient *A* (1.01 ± 0.83 L m⁻² h⁻¹ bar⁻¹) and salt permeability coefficient *B* (0.19 ± 0.19 L m⁻² h⁻¹) values similar to the mLbL membranes created in this work. Both sets of 60-cycle mLbL polyamide membranes also have comparable membrane transport properties to interfacially polymerized thin-film composite polyamide membranes that were characterized using the same technique [5], demonstrating their suitability as model materials for conventional interfacially polymerized polyamide membranes.

2.2. Membrane test cell

A membrane test cell was designed with feed solution and draw solution channels on either side of the membrane sample so that forward osmosis permeation could be imaged by neutron radiography. The width of the channels (0.8 cm) represents a compromise between reducing the membrane sample width to improve imaging and maintaining adequate membrane area to observe realistic forward osmosis permeation. The membrane test cell was fabricated from aluminum,



Fig. 2. Illustration and photographs of the membrane test cell fabricated for neutron radiography experiments. The test cell was machined from aluminum with feed solution and draw solution channels. Thin-film composite membrane samples, comprising a polyamide selective layer and a polysulfone or polycarbonate support layer, are sealed in the cell with poly(tetrafluoroethylene) o-rings. The membrane selective layer is oriented facing the feed solution and the support layer is oriented facing the draw solution.

which facilitates imaging due to its small neutron attenuation coefficient. The membrane sample was sealed against the feed and draw solution channels with poly(tetrafluoroethylene) o-rings, a material that also has a relatively small neutron attenuation coefficient. The membrane test cell and operating configuration are illustrated in Fig. 2.

2.3. Neutron radiography experiments

2.3.1. Neutron Imaging Facility at the NIST Center for Neutron Research

Neutron radiography experiments were conducted at the National Institute of Standards and Technology (NIST) Center for Neutron Research (NCNR) (Gaithersburg, MD, USA). The neutron source is a 20-MW heavy-water fission reactor that produces thermal neutrons. The Neutron Imaging Facility views the center of the reactor through a beam flight tube that is approximately 6 m long [30]. To approximate a neutron point source, a slit aperture 1 mm wide \times 1 cm long was used to define the beam for the radiography experiments. The resulting collimation ratio (L/D) was approximately 6000 with a neutron flux of 8.0×10^5 cm⁻² s⁻¹ [31]. At the end of the beam tube, the sample is placed immediately in front of the detector and mounted to a motorized stage with movement in x, y, and z directions. The detector is a gadolinium oxysulfide (GadOx) scintillator plate coupled with a scientific complimentary metal-oxide semiconductor (sCMOS) camera [31]. A schematic of the experimental configuration used for studying forward osmosis permeation at the Neutron Imaging Facility is shown in Fig. 3.

Neutron radiography experiments were designed to image light elements, such as hydrogen and lithium, which are poorly imaged by Xrays and other techniques. Neutron radiography is an effective imaging technique for these light elements because neutrons interact with matter primarily via the nucleus rather than via the electron cloud [32]. Furthermore, the distribution of this neutron interaction among elements is not a smooth function of atomic number [33]. Consequently, imaging contrast can be achieved between elements with proximate atomic numbers and even between isotopes of the same element [32]. Neutron radiography has been previously used for non-destructive testing of industrial components, studying water and ion transport in fuel cells and lithium batteries, respectively, and imaging fluid flow in porous media [32]. Neutron radiography data have also been used to validate the performance of numerical models for predicting water formation and transport in polymer electrolyte membrane fuel cells



Fig. 3. Schematic of the neutron imaging configuration for studying forward osmosis permeation. A collimated neutron beam (collimation ratio, L/D = 6000 in the direction of membrane sample width) is directed at a membrane sample during forward osmosis permeation, resulting in a transmitted image of beam intensity.

[34].

2.3.2. Image collection

Neutron radiography experiments were conducted in three parts to image membrane samples during forward osmosis permeation, as summarized in Table 1.

Materials were selected for the experiments to maximize the neutron attenuation of the draw solute and minimize the attenuation of the other sample materials. Neutron transmission through a sample is described by the Lambert-Beer law that assumes a constant neutron flux from a point source [35]:

$$T = \frac{I}{I_0} = e^{-\mu t} \tag{3}$$

The parameter *T* is neutron transmission, *I* is the beam intensity when imaging the object of interest, I_0 is the beam intensity of a reference state, μ is the total neutron attenuation coefficient of the material, and *t* is the material thickness through which the neutron beam passes. According to Eq. (3), neutron attenuation by both neutron scattering and neutron absorption is described by the total neutron attenuation coefficient. High neutron attenuation in a sample results in low transmission, and a corresponding high optical density (optical density = μ t). The relative sizes of neutron attenuation coefficients, which include relative number densities, for the different elements comprising the materials used in this work are hydrogen, H > lithium, Li > chlorine, Cl > > deuterium, D > carbon, C > oxygen, O > fluorine, F > aluminum, Al [36].

Lithium chloride (LiCl) was used as the draw solute and either deionized water (H_2O) or deuterium oxide (D_2O , heavy water) were used as solvents in the permeation experiments. Water and LiCl are highly visible in neutron radiography because of their relatively large neutron attenuation coefficients, but heavy water has a relatively small neutron attenuation coefficient. Consequently, heavy water was used as a solvent for the LiCl draw solution so that the attenuating properties of LiCl would not be obscured, and LiCl concentrations could be observed across the membrane feed and draw solution channels.

During the permeation experiments, feed and draw solutions were pumped at 2 mL min^{-1} flow rates, which resulted in a cross flow velocity of 0.1 cm s⁻¹ and laminar flow conditions within the membrane test cell. The same membrane test cell and flow conditions were also used to characterize membrane transport properties. An estimated permeate flux of $16.7 \text{ L m}^{-2} \text{ h}^{-1}$ was achieved for the polyamide and polycarbonate composite membranes using a 1.5 mol L^{-1} LiCl draw solution.

In neutron imaging, a tradeoff exists between reducing exposure time for better temporal resolution and improving the spatial resolution

Table 1

Experimental plan, feed solutions, and draw solutions used for neutron radiography study of forward osmosis permeation.

Experiment part	Purpose	Feed solution	Draw solution
1	Observe wetting behavior of membrane support layer.	Heavy water (D ₂ O) Deionized water (H ₂ O)	Heavy water (D ₂ O) 1.5 mol L ^{-1} lithium chloride (LiCl) in heavy water (D ₂ O)
3	Rinse test cell to prepare for next membrane sample.	Deionized water (H_2O)	Deionized water (H_2O)

[32]. The temporal resolution of neutron imaging is determined by the neutron flux and the readout time of the detection system. Spatial resolution is affected by image blur, detector limitations, and camera optics [37]. The impact of the collimation ratio on both image blur and neutron flux illustrates the interdependence of the temporal and spatial resolution. The collimation ratio (L/D) is defined as the ratio of the distance between the detector and the neutron beam-defining aperture (L) and the size of the aperture (D) [32]. Image blur is a function of this collimation ratio [33]:

$$d = \ell \left(\frac{L}{D}\right)^{-1} \tag{4}$$

where *d* is the image blur, *l* is the separation distance between the sample and the detector, and (L/D) is the collimation ratio. The image blur may be reduced by increasing the collimation ratio, such as reducing the size of the beam-defining aperture. However, the neutron flux scales as $(L/D)^{-2}$, and increasing the collimation ratio increases the exposure time required to obtain the same neutron image. A factor of two improvement in image blur results in a factor of four increase in image exposure time [30].

We achieved image spatial resolutions of $<10\,\mu m$ by using the smallest beam aperture to maximize the collimation ratio. The resulting temporal resolution was diminished, and we determined that thirty neutron images (2560 pixels \times 2160 pixels) at an exposure time of 90 s per image were necessary for each membrane sample under each experimental condition.

Before commencing imaging, the membrane test cell was aligned in the neutron beam by minimizing the apparent thickness of the membrane sample, which was oriented in a plane parallel to the beam. Prior to introducing feed or draw solutions to the test cell, dark field and flat field images were collected. The dark field images were captured with the beam shuttered to measure background intensity. Flat field images, which represent the reference state beam intensity (I_o), were collected with the dry test cell, including the membrane sample.

The first part of the radiography experiments involved flushing the feed and draw solution channels with heavy water to wet the membrane and remove air bubbles in the flow channels. A series of images were collected with heavy water flowing through the test cell to observe the wetting behavior of the membrane support. Next, water feed solution and a draw solution of 1.5 mol L^{-1} LiCl in heavy water were introduced to the test cell to initiate permeation. Finally, the system was flushed with deionized water to prepare for the next membrane sample.

2.3.3. Image analysis

Images from neutron radiography were processed to remove noise and to calculate the optical density. Image analysis was performed with a custom image processing routine developed at NIST [30]. A flow chart illustrating the image analysis process is shown in Fig. 4. First, groups of three sequential images from the 30 raw images collected at each experimental condition were median combined to remove noise, resulting in ten images [33]. A spatial median filter was then applied to the ten combined images to further reduce noise. A kernel size of 3×3 was used so that each pixel in the combined image was assigned the median value of the surrounding 3×3 pixel area [32]. The ten combined and filtered images were then averaged to create a single image of each experimental condition for each membrane sample.

Optical density (OD) was calculated from the beam intensity (I) of

the averaged images:

$$OD = -\ln(T) = -\ln\left(\frac{I}{I_0}\right) \tag{5}$$

The incident beam intensity (I_0) was represented by the intensity of the flat field image of the dry membrane test cell. Background dark field images were subtracted from averaged experimental images and from the reference flat field image before calculating optical density [33]. Both dark field and flat field images were processed from 30 raw images, as described in Fig. 4. To account for variations in the neutron reactor output over time as the images were collected, the optical density calculations were scaled to a region of the aluminum test cell that was apparent in each image but that was not exposed to different feed and draw solutions [33].

The resulting optical density images were divided into eight columns of equal horizontal width that spanned vertically across the image from feed solution channel to draw solution channel. An average optical density profile was calculated for each column by averaging the optical density values of each horizontal row of pixels. Measurement uncertainty was represented by the root mean squared value of optical density for each row of pixels. LiCl concentrations were calculated across the membrane feed solution and draw solution channels using these average optical density profiles.

2.3.4. Calibration curve for optical density and LiCl concentration

LiCl draw solution concentration was related to optical density measurements through a calibration curve. To construct the calibration curve, a stepped cuvette made of aluminum, shown in Fig. 5A, was imaged with different solution concentrations of LiCl in heavy water. An example neutron image of the cuvette is shown in Fig. 5B. After image processing, the optical density was calculated for each LiCl solution concentrations and step thickness. For the calibration curve, LiCl solution concentrations and step thicknesses were converted to the quantity of LiCl ions imaged per pixel, based upon the $6.5 \,\mu\text{m}$ pixel resolution of the image. The resulting calibration curve, shown in Fig. 5C, relates optical density (*OD*) to LiCl content (mol):

$$OD = a(LiCl \ content \ (mol))^2 + b(LiCl \ content \ (mol))$$
(6)

where $a = -7.82 \times 10^{17}$ and $b = 2.20 \times 10^{9}$. The quadratic fit of the calibration curve reflects the beam hardening effect that results from energy-dependent attenuation behavior of the polychromatic neutron source [35]. Lower energy neutrons are more attenuated than higher energy neutrons, and the transmitted neutron beam is more energetic than the incident beam as a result of this hardening effect [30].

Calibrating optical density to LiCl content allows for the concentration of LiCl [*LiCl*] solutions at different image resolutions and resulting pixel volumes to be calculated from optical density (*OD*) measurements:

$$[LiCl] (mol \ L^{-1}) = \frac{LiCl \ content \ (mol)}{pixel \ volume \ (L)}$$
(7)

where pixel volume refers to the area of each pixel in the image multiplied by the sample thickness through which the beam was transmitted.

Eq. (6) and Eq. (7) were used to calculate LiCl concentrations in the feed solution and draw solution channels from optical density measurements made during forward osmosis permeation experiments. The

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Fig. 4. Flow chart illustrating the image processing routine for neutron radiography image analysis. A) Raw neutron intensity images (n = 30) are B) median combined in sequential groups of three. C) The combined images (n = 10) are spatially median filtered with a kernel size of 3×3 pixels. D) Combined and filtered neutron intensity images (n = 10) are averaged and rotated to a horizontal position if necessary. E) Neutron transmission (*T*) is calculated from the averaged neutron intensity image by subtracting the dark field intensity from the averaged neutron intensity and dividing by the flat field intensity, from which the dark field intensity has also been subtracted. F) Optical density is calculated from neutron transmission (*-*(*n*(*T*)), and optical density profiles are averaged across the membrane image from feed solution channel to draw solution channel.



Fig. 5. Calibration of lithium chloride content to optical density. A) Photograph of the stepped cuvette used to measure the optical density of varying thicknesses of draw solutions with different concentrations of lithium chloride in heavy water. B) Representative optical density image of the stepped cuvette. C) Plot of optical density for different lithium chloride contents through which the neutron beam was transmitted. The dashed line represents a quadratic calibration curve fit to the data.

membrane samples were located farther from the detector than the stepped cuvette because of the membrane test cell geometry. Consequently, the resulting pixel resolution of the images was 8.5 μ m, and the pixel volume was 5.78×10^{-10} L. The calculated LiCl concentration profiles across membrane feed and draw solution channels observed during neutron imaging were then compared to predicted concentrations from the standard film model.

3. Results and discussion

3.1. Incomplete wetting of polysulfone support layer

Optical density images of the polyamide and polysulfone composite membrane show the presence of air bubbles throughout the membrane thickness. Fig. 6 shows a representative optical density image, where air bubbles appear as dark areas because of their low neutron attenuation and low optical density. The presence of air bubbles is visual confirmation of the incomplete support layer wetting that has been



Fig. 6. Schematic of membrane test cell and representative optical density image of a polyamide and polysulfone composite membrane that is experiencing incomplete wetting of the polysulfone support layer. The inset illustrates the reduction in wetted porosity for permeation that results from the presence of air bubbles in the membrane support layer. Scale bar in optical density image is 1 mm.

proposed for hydrophobic polysulfone membrane supports [15–17]. The resulting reduction in wetted porosity would reduce effective membrane area and impact estimates of membrane transport properties.

This visual confirmation of incomplete support layer wetting emphasizes the importance of conducting a wetting procedure before using a membrane in forward osmosis, such as the isopropanol wetting that is prescribed in a standard protocol for testing forward osmosis membranes [14]. Neutron radiography may serve as a tool to investigate the efficacy of support layer wetting protocols and support layer modifications, such as hydrophilic coatings and polymer blends, for removing air bubbles and maximizing wetted porosity in the support.

3.2. Dilutive external draw solution concentration polarization

Significant dilutive external draw solution concentration



Fig. 7. A) Lithium chloride (LiCl) draw solution concentration profile calculated from neutron images of forward osmosis permeation with a polyamide and polycarbonate composite membrane. Red circle symbols indicate the mean value and gray error bars extend to \pm root mean squared value as an indicator of measurement uncertainty. The membrane is located at position 0 mm on the horizontal axis, and the feed and draw solution channels are located on the left and right of the membrane, respectively. Observations from position -2 mm in the feed solution channel to position 2 mm in the draw solution channel have been omitted as shown by the break in the horizontal axis. Dilutive external draw solution concentration polarization is apparent in the decrease in LiCl concentration from 1.5 mol L⁻¹ at position 3.5 mm to 0.15 mol L⁻¹ at position 2 mm. B) Comparison of the observed LiCl draw solution concentration profile predicted by the standard thin-film model for forward osmosis permeation (black long-dash line), a revised film model including an external draw solution boundary layer (blue short-dash line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

polarization (ECP_D) is apparent in LiCl concentration profiles calculated from neutron images of forward osmosis permeation with the polyamide and polycarbonate composite membrane. A representative observed LiCl draw solution concentration profile is shown in Fig. 7A with a dilutive concentration polarization boundary layer approximately 1.5 mm thick. This draw solution concentration polarization outside of the membrane support layer is not accounted for in the standard thin film model (Eq. (1)), which attributes all draw solution dilution to internal concentration polarization (ICP_D) within the membrane support. As a result, for the forward osmosis experimental conditions imaged in Fig. 7A, the standard film model would overestimate the membrane support layer structural parameter, a phenomenon that has been previously reported [20].

The presence of air bubbles also posed a challenge for the experiments using a polyamide and polycarbonate composite membrane to observe LiCl draw solution concentrations. In these experiments, the existence of air bubbles in the regions of the feed and draw solution channels adjacent to the membrane significantly affected the transmitted neutron intensity. The combination of non-uniformly distributed air bubbles and the different neutron attenuation coefficients of the multiple materials present in this region (air bubbles, poly(tetrafluoroethylene) o-rings, LiCl draw solution) resulted in convoluted neutron intensity measurements that could not be related to LiCl concentration. Consequently, neutron radiography measurements from a 2 mm region on both the feed and draw solution sides of the membrane have been omitted from analysis, as shown in Fig. 7. Future experiments will focus on minimizing the number of different neutron-attenuating materials present in the imaging area by sealing the test cell without o-rings.

The observed draw solution behavior ($ECP_D = 0.10$) illustrates that the assumption of negligible ECP_D in the standard film model is not accurate for the conditions of this experiment. The extent of the ECP_D boundary layer may have been exacerbated by the low flow conditions within the membrane test cell (cross flow velocity = 0.1 cm s^{-1}), and it could possibly indicate damage to the membrane selective layer that is causing a high reverse draw solute flux. Irrespective of the confounding aspects of low flow and potential membrane damage, the observed LiCl concentrations from neutron imaging experiments demonstrate the need for different transport models that include the ECP_D boundary layer and that employ mass transfer coefficients that accurately describe the flow conditions within the membrane test cell.

3.3. Evaluation of alternatives to standard transport model

To demonstrate the utility of neutron radiography for studying membrane transport, we used alternative models of forward osmosis permeation to calculate LiCl draw solution concentration profiles and compared them to the observed concentration profile, as shown in Fig. 7B and summarized in Table 2. In all the evaluated transport models, the experimentally determined membrane water and solute permeability coefficients were fixed, and the support layer structural parameter *S* was varied to achieve the estimated permeate flux of $J_w = 16.7 \text{ Lm}^{-2} \text{ h}^{-1}$. The performance of the alternative transport models was assessed by comparing the simulated LiCl draw solution concentrations and boundary layer thicknesses to those observed from neutron imaging and by comparing the estimated support layer structural parameter to the known value of $S = 200 \,\mu\text{m}$ calculated from Eq. (2).

The LiCl draw solution concentration profile estimated from the standard film model approximates osmotic pressure from concentration using the van't Hoff equation, and it does not include an ECP_D boundary layer. The van't Hoff approximation has been identified as a potential source of error in the standard film model [22]. Therefore, in the alternative transport models evaluated, osmotic pressure of the bulk draw solution was determined using OLI Analyzer electrolyte modeling software (version 9.0, OLI Systems, Inc.), which resulted in an increase in estimated osmotic pressure from 74.3bar to 87.4 bar for the 1.5 mol L⁻¹ LiCl bulk draw solution.

Bui et al. proposed a revised film model for forward osmosis permeation that includes an ECP_D boundary layer in the draw solution [11]. This "draw boundary layer model" estimates ECP_D using a mass transfer coefficient based upon the same Sherwood correlation as used to estimate ECP_F in the feed solution channel. The estimated draw solution concentration profile from the draw boundary layer model is shown as the blue short-dash line in Fig. 7B, and it includes 0.33 mm thick boundary layers on both the feed and draw solution sides of the membrane. ECP_D in the draw boundary layer model is so significant that draw solution concentration must increase within the support layer, resulting in a negative structural parameter value, in order to achieve the necessary osmotic pressure at the draw solution side of the 1

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ort modelMast transferFed solution concentrative external coefficient, k (m/s)ECPboundary layerDraw solution dilutive external concentrationECPboundary layerStructural parameter, S (m)td film model [5] 3.94×10^{-6} 3.23 3.23×10^{-6} 3.23 0.33 0.33 0.49 $ 200$ td film model [6] 3.94×10^{-6} 3.23 0.33 0.33 0.33 $ 200$ oundary layer 3.94×10^{-6} 3.23 0.33 0.33 0.33 0.33 $ -$ oundary layer 6.76×10^{-6} 1.98 0.17 0.83 0.33 0.33 $ -$ oundary layer 6.76×10^{-6} 1.98 0.17 0.83 0.50 0.17 48 oundary layer 6.76×10^{-6} 1.98 0.17 0.83 0.50 0.17 48								
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undary layer $_{6.76\times10^{-6}}$ 1.98 0.17 0.83 0.50 0.17 48 el with revised k 9]	undary layer el [6]	3.94×10^{-6}	3.23	0.33	1.35	0.31	0.33	- 84
	undary layer el with revised <i>k</i> 9]	6.76×10 ⁻⁶	1.98	0.17	0.83	0.50	0.17	48

Comparison of transport models used to model forward osmosis permeation experiments

Table 2

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membrane selective layer to drive permeation. The significant EPC_D in this draw boundary layer model results from the relatively low mass transfer coefficient k. The conventional Sherwood correlation for the mass transfer coefficient is based upon laminar flow through a nonporous system [38], which does not account for permeation through the membrane that serves as one wall of the flow channel. Applying a different Sherwood number relationship to estimate the mass transfer coefficient considering the effect of permeation through the membrane [39], the mass transfer coefficient k is increased, and associated *ECP* boundary layers are reduced to 0.17 mm thick. The estimated LiCl draw solution concentration profile using this "draw boundary layer model with revised k" is shown as the green dot-dash line in Fig. 7B.

The mass transfer coefficients used in each transport model referenced in Fig. 7B are included in Table 2, and the resulting estimated concentration polarization moduli, boundary layer thicknesses, and support layer structural parameters are summarized. The alternative transport models represent the observed ECP_D behavior more accurately than does the standard film model. However, none of the models approximates the significant extent of ECP_D that was observed. The discrepancy between observed and modeled results may also reflect the challenges of low flow conditions and potential membrane damage discussed in Section 3.2.

4. Conclusions

Neutron radiography is a quantitative measurement tool for studying water and solute transport through desalination membranes by allowing direct visual observation of solute concentrations in the membrane boundary layers. We applied neutron radiography to investigate two challenges that hinder accurate transport modeling of the forward osmosis process: incomplete membrane support layer wetting and overestimation of the support layer structural parameter. Observations from neutron radiography confirm the presence of air bubbles in the membrane during forward osmosis permeation and reveal the development of significant dilutive external concentration polarization in the draw solution. Both phenomena affect forward osmosis transport, but neither is accounted for in the standard film model.

Our results demonstrate the importance of direct experimental observations for evaluating and refining forward osmosis transport models, which is an area of active research. The observation of incomplete support layer wetting also validates the necessity of ongoing work to develop new hydrophilic materials for forward osmosis membrane support layers. Neutron radiography can serve as a tool to evaluate the performance of these new materials and the efficacy of membrane wetting protocols. While our initial work has focused on the forward osmosis process, neutron radiography may also be applied to study other transport phenomena in a variety of membrane separation processes, such as investigating pore wetting in membrane distillation, the performance of different spacer designs for promoting mass transfer in crossflow membrane modules, and the contribution of cake-enhanced concentration polarization to permeate flux decline during fouling of desalination membranes. Our future work with neutron radiography will incorporate improvements to the membrane test cell design to eliminate o-rings and improve mass transfer in the feed and draw solution channels. We intend to apply the technique to higher crossflow rates and larger membrane areas to more closely approximately bench-scale membrane testing conditions.

Acknowledgments

This work was supported by the U.S. Department of Commerce, the NIST Radiation Physics Division, the Director's Office of NIST, and the NIST Center for Neutron Research. The authors acknowledge the assistance of Mr. Eli Baltic in setting up and conducting the experiments at the Neutron Imaging Facility.

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