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pH Sensitivity of Ion Exchange through a Thin Film Composite Membrane in Forward Osmosis

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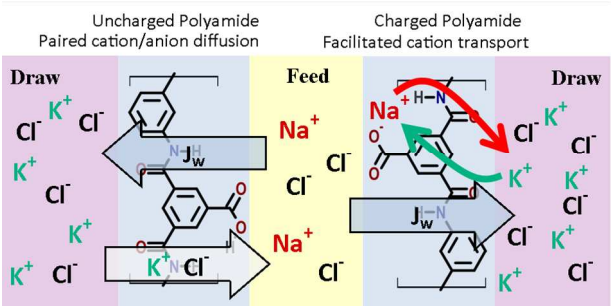
Abstract: The uneven permeation of cations and anions through forward osmosis membranes offers a new technical challenge in the development of forward osmosis processes. Cation exchange in polyamide thin film composite membranes is caused by carboxylic acid functional groups within the structure of these membranes' selective layers. These functional groups will gain or lose a proton depending on the external solution pH. The deprotonation of a polyamide at alkaline pHs results in a net negative charge, allowing for the exchange of cations between feed and draw solutions having monovalent cations. In this study the importance solution pH and its influence on cation transport across a commercial thin film composite forward osmosis membrane was examined. It was found that cation transport across this membrane varies significantly with changes in pH and occurred fastest at alkaline pH.

TOC Art


Uncharged Polyamide
Paired cation/anion diffusion
Charged Polyamide
Facilitated cation transport
Draw
Feed
Draw
Na+
Cl-
K+
Jw

1. Introduction

Forward osmosis (FO) processes use an osmotic pressure gradient to drive water flux across a semi-permeable membrane[1,2,3]. A critical part of FO process design is draw solute selection[4-11]. In a FO process, suitable draw solutes need both high solubility and diffusivity to effectively exert osmotic pressure across asymmetric semi-permeable membranes. Electrolyte draw solutes have become common in many large-scale applications of FO processes[12-14]. Opposite draw solute selection in FO process design is membrane selection. Membranes tailored for FO need to have high permselectivity and low structural parameter to allow for efficient water transport across an asymmetric membrane[15,16]. Cellulose triacetate (CTA) was used to form the first membrane designed specifically for FO[4,17,18]. In an effort to improve performance, thin film composite (TFC) membranes have been introduced as a new platform for FO membrane design[2,19,20]. Amongst the advantages of TFC membranes is higher water permeance at similar selectivities and hydrolytic stability[21,22].

The polyamide selective layer of a TFC membrane is commonly made from the reaction of trimesoyl chloride (TMC) and m-phenylenediamine (MPD)[23]. The reaction yields a partially cross-linked structure with the TMC monomer forming two or three amide bonds[24]. TMC monomers that form only two amide bonds have a third acyl chloride that does not form an amide bond[24,25]. This remaining acyl chloride group later hydrolyzes to a carboxylic acid. Carboxylic acid functional groups deprotonate at alkaline pH, imparting a negative charge that may facilitate the transport of cations through the polyamide[26,27]. In RO membranes using this chemistry, the charge aids in salt rejection since the negative charge repels anions (like chloride). Charge neutrality requires that the membrane need only reject one ion since cations

cannot cross without their counterion. In FO processes that employ an electrolyte draw solution, cations from the feed solution may move across the negatively charged polyamide without their counterion, maintaining electroneutrality by exchanging with cations within the draw solution[18,26,28].

Evidence of cation exchange is observed as disparate forward cation and anion fluxes or high forward and reverse flux of a single ionic species. This behavior has been observed under neutral and alkaline conditions between monovalent cations[18,26,28]. A similar ion exchange behavior has been observed for the CTA membrane with anions when the draw or feed solution contains nitrate[29,30]. One notable study by Lu et al. observed some of the sensitivity of these functional groups to pH differences across a thin film composite membrane using ammonium chloride as a draw solute and a feed solution of sodium chloride at a pH of 3 and 6. Ammonium chloride in solution has a pH of 4.5. Ion exchange observed occurring across the commercial FO membrane did so with a pH gradient across the membrane. This caused the draw solution to have a pH below and the feed solutions to have above the pK_a of the carboxylic acid functional groups[28]. Elsewhere pH gradients across cellulose triacetate FO membrane have been observed influencing the transport of propanoic acid into a feed solution of DI water with the sharpest difference in propionic acid transport occurred over a narrow pH range (i.e. pH=pKa±2)[31]. In regards to Lu et al. this means that the pH gradient across the membrane's selective layer which with a weak electrolyte[28] may influence cation transport through selective layer permeation as a neutral species (i.e. as ammonia) and with the pH gradient speciating back to ammonium and forcing the back diffusion of sodium in a mechanism hypothesized by Arena et al[26].

To date, no study has included a systematic observation of forward and reverse cation transport in the absence of a pH gradient across the membrane using strong acid/strong base electrolytes. The choice of strong strong acid/strong base electrolytes eliminates the existence of neutral species and allows for pH control by buffering the feed and draw solutions to influence membrane properties. The objective of this study is to concretely show that cation/membrane interactions are the driving force of cation exchange in forward osmosis.

2. Materials and Methods

2.1. Materials

The membrane used in this study is a commercial TFC FO membrane from Hydration Technology Innovations (HTI). This membrane is later referred to as the TFC. The feed and draw solutes used in this study were sodium chloride and potassium chloride (Fisher Scientific, Pittsburgh, PA). The draw and feed solutions were buffered using, Bistris and CAPS buffer purchased from Fisher Scientific (Pittsburgh, PA), Citric acid monohydrate purchased from Acros Organics (Geel, Belgium) and Tris buffer purchased from Sigma Aldrich (St. Louis, MO). pH was adjusted using hydrochloric acid (Sigma Aldrich, St. Louis, MO), potassium hydroxide (Acros Organics, Geel, Belgium), and sodium hydroxide (Fisher Scientific, Pittsburgh, PA). Water used in this study was ultrapure Milli-Q (18.2MΩ) water produced by a Millipore Integral 10 water system, (Millipore Corporation, Billerica, MA).

2.2. Membrane physicochemical properties

2.2.1. Scanning electron microscopy

The top and cross-section images of the TFC membrane, coated with a thin layer of gold, were obtained using JEOL 6335F Field Emission SEM (JEOL USA, Inc. Peabody, MA). To obtain cross sectional images, the membrane was soaked it in ethanol, followed by hexane, and immersed into liquid nitrogen. While frozen, the membrane was fractured and the woven mesh was cut closely to the fractured edge.

2.2.2. Fourier transform infrared spectroscopy

The TFC membrane was evaluated using Fourier transform infrared (FTIR) spectroscopy to identify key functional groups of the membrane's selective layer and verify the presence of a polyamide selective layer. The FTIR analysis was performed on a dried membrane sample using A Thermo Scientific (Waltham, MA) Nicolet iS10 FTIR spectrometer with a Smart iTR attachment. Measurements were taken of the membrane's selective layer using 64 scans with a resolution of $4cm^{-1}$.

2.3. Ion transport in forward osmosis

2.3.1. Forward osmosis testing

The feed and draw solutions were buffered at identical pH of 2, 4, 6, 8, and 10. Potassium chloride was selected as a model draw solute to serve as an analog for draw solutions proposed for forward osmosis processes[4,7,15,26,32]. Using potassium chloride eliminates draw solutes containing a weak acid or weak base and ensures ensures easy quanitification using atomic absorption spectroscopy[33,34].

Forward osmosis tests were performed on a laboratory scale FO system in the FO mode using a buffered draw solution of 1.0M potassium chloride with feed solutions of only buffer and buffered 0.1M sodium chloride. These solutions were circulated counter-current in bench-scale forward osmosis test systems with a cross flow velocity of $0.25 m \cdot s^{-1}$ at 20±0.5°C. For these tests the membrane support layer was in contact with the potassium chloride draw solution (FO mode)[32]. Water flux and reverse potassium flux were observed sequentially for feed solutions consisting of only buffer and 0.1M buffered sodium chloride. Forward sodium flux was observed when the feed solution was buffered 0.1M sodium chloride. FO experiments were begun by monitoring water flux across the membrane using a feed solution of buffer only. After the first hour, the feed solution was adjusted to a concentration of 0.1M sodium chloride. Water flux was monitored for at least two additional hours using the buffered 0.1M sodium chloride feed solution.

2.3.2. Measurement of ion concentrations

The feed and draw solutions were analyzed for potassium and sodium concentration, respectively. Samples of the were extracted prior to the addition of sodium chloride to the feed solution and at the end of the test. Initial samples of the feed solution were taken when potassium hydroxide was needed to adjust the pH (i.e. the pH 4 and pH 10 tests). Potassium and sodium concentrations were measured by direct aspiration atomic absorption (AA) spectrophotometry on a Thermo Scientific ICE 3000 atomic absorption spectrometer (Thermo Scientific, Nashua, New Hampshire) equipped with a combination potassium/sodium hollow cathode lamp. The solutions were analyzed according US EPA method 700B which has a lower detection limit of 0.01 mg/L and 0.002 mg/L and a sensitivity of 0.04 mg/L and 0.015 mg/L for

potassium and sodium respectively[35]. Some samples required significant dilution so that they were in the measurable range of the instrument. The measured concentrations of sodium and potassium within these solutions were used to determine the total mass of potassium within the feed and sodium within the draw. The change in mass was divided by the time interval between sample extraction, molar mass, and membrane surface area to calculate the forward (in the direction of water flux) sodium and reverse (opposite the direction of water flux) potassium molar fluxes.

3. Results and Discussions

3.1. Membrane physicochemical properties

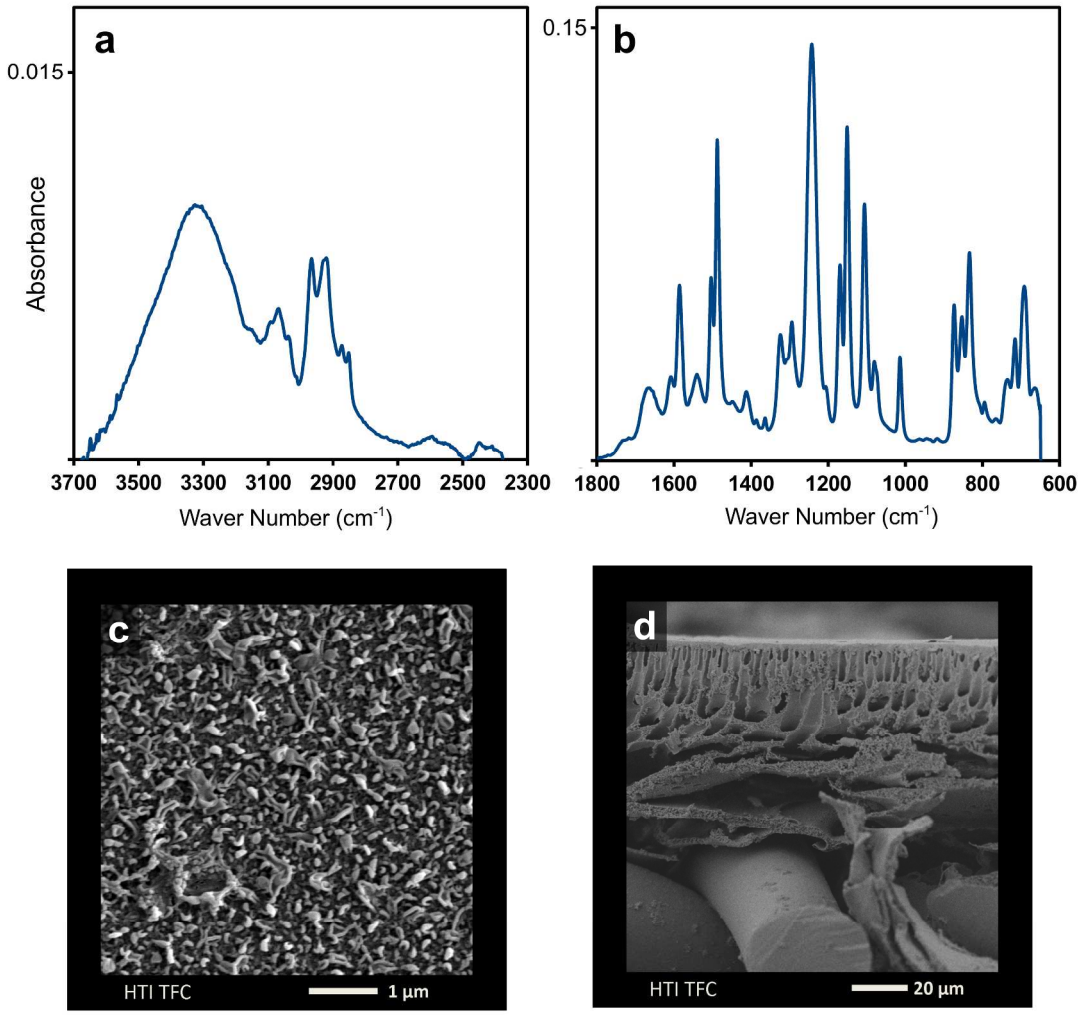


Fig. 1. FTIR spectra of the TFC FO membrane at wave numbers of 2300-3700cm^{-1} (a) and 600-1800cm^{-1} (b). SEM images of the structure of the TFC membrane's selective layer (c), support layers (d).

Fig. 1 shows the chemical and morphological characteristics of the membrane used in this study. The TFC membrane's selective layer has an FTIR spectrum which has been characteristically attributable to a fully aromatic polyamide. This membrane shares peaks which have been noted previously by Ren and McCutcheon at 1655cm^{-1}, 1610cm^{-1}, and 1545cm^{-1} (Fig. 1b) for an earlier iteration of this TFC FO membrane[19]. Additionally available patent literature

states that the polymerized selective layer was formed m-phenylenediamine (MPD) and trimesoylchloride (TMC)[36] further suggesting the presence of carboxylic acid functional groups characteristically present within the partially cross-linked structure of a TFC membrane's polyamide[37]. The carboxylic acid functional group would give this membrane an isoelectric point around pH 5 which has been observed by Tang et al. who characterized different permselective RO membranes in streaming potential[38]. In addition to the FTIR spectra, the TFC also possess the rough surface morphology which has been noted in other studies characterizing the polyamide selective layers of TFC membranes for both forward and reverse osmosis (Fig. 1c)[19,40].

3.2. pH dependence of water and ion flux in forward osmosis

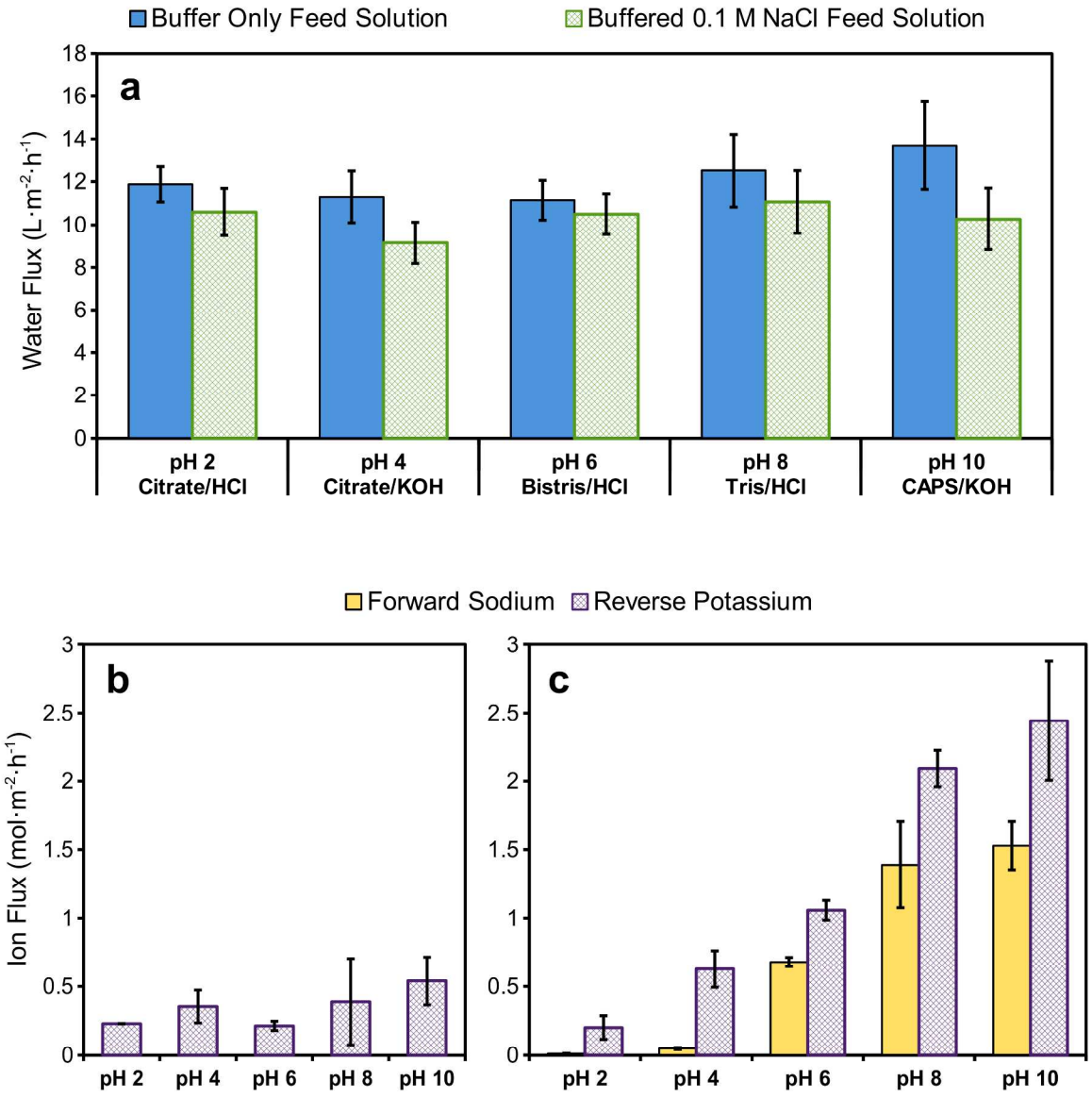


Figure 2. Observed water flux for a 1.0M potassium chloride draw solution using feed solution of only buffer and buffered 0.1M sodium chloride at a pH of 2-10 (a). Observed ion flux for a 1.0M potassium chloride draw solution using a feed solution of only buffer (b) and buffered 0.1 M sodium chloride (c). Temperature 20°C and 0.25m·s^{-1} cross-flow velocity.

The water and solute fluxes across the TFC as affected by draw and feed solution pH are shown in Fig. 2. These data encompass a number of interesting findings both in contradiction

and agreement to those previously reported. Water flux did not change significantly with pH, coinciding with behavior that has been observed for polyamide TFC membranes in reverse osmosis[37,44]. These same studies noted an increase in sodium chloride rejection (decreased solute permeability) at more alkaline pH[37,44]. Translating this to FO, a decrease in solute permeability would also decrease the reverse solute flux[45]. Potassium reverse flux for a feed solution of only buffer appears to follow no clear trend with respect to pH (Fig. 2b). It remains statistically flat from pH 2-8, only showing a significant increase at pH 10. This contradicts any premise that the solute permeability of this membrane should decrease with increasing pH, as a decrease in the solute permeability should also decrease the reverse solute flux of potassium. The potassium reverse flux represents potassium chloride flux when the feed solution contains only buffer. There is no concentration difference of buffer between the feed and draw solutions, so potassium that crosses the membrane selective layer must carry chloride with it to maintain electroneutrality between the feed and draw solution[18,29,46,47].

There is only a slight decrease in water flux upon addition of sodium chloride to the feed solution. This parallels more significant drops in water flux noted when comparing water flux observed with a feed solution of deionized water to water flux observed with a 0.25M sodium chloride using the ammonia-carbon dioxide draw solution[26]. The lack of a substantial drop in water flux upon addition of sodium chloride to the feed is likely due to the buffer within the feed solution. Although the bulk buffer concentrations are equivalent, they do exert osmotic pressure and more importantly are impacted by external concentration polarization (ECP). ECP will reduce flux by increasing the buffer selective layer concentration reducing the osmotic pressure difference across the membrane. This makes for a less noticeable drop in water flux

when the feed solution is changed from only buffer to a buffered 0.1 M sodium chloride solution.

Large differences can be observed in the forward solute flux of sodium and reverse solute flux of potassium with increasing pH. Sodium flux at pH 2 & 4 is two orders of magnitude lower than sodium fluxes are at pH 10. This change must be strongly influenced by carboxylic acid functional groups within the selective layer. Polyamide selective layers which have been analyzed by zeta potential show neutral charges at pHs between 4-6[27,28,48,49]. Similar results have been noted by contact angle titration, which measures the contact angle of a buffered solution dropped onto a polyamide[48,50]. As pH increases carboxylic acid functional groups deprotonate (–COOH becomes $–COO^-$), increasing negative charges on the membrane's surface. If homogeneity within the polyamide is assumed, increasing negative charges on the selective layer surface would correspond to increasing negative charges within the membrane's selective layer, since the pH is constant on both sides of the selective layer. The increasing number of negative charges will increase cation transport across the polyamide. This is demonstrated in Fig. 2c where a sharp increase in forward and reverse cation flux is observed at higher pH. Cation transport will be limited by the available negative charges within the polyamide (to maintain local electroneutrality). The physical structure of the polyamide will impose a limit on the rate of cation exchange across the polyamide (by the number of carboxylic acid functional groups in the polyamide structure). Such a maximum may occur at pH greater than 8, as forward and reverse cation flux are statistically similar between pH 8 and 10 (Fig. 2c).

Potassium flux was higher than the sodium flux across the range of studied pH. The difference between the forward sodium flux and reverse potassium flux (Fig. 2c) is

approximately equivalent to the reverse potassium flux where the feed solution is only buffer (Fig. 2b). This indicates that the reverse potassium flux using buffered 0.1 M sodium chloride feed solution encompasses both Fickian diffusion and facilitated transport between the feed and draw solutions. Dual paths for solute transport create a complicated design challenge in FO membrane selective layer development. Low solute permeabilities (to anion/cation pairs) are needed as well as the development of selective layer chemistries lacking charged functional groups which contribute to ion transport at process conditions.

Supporting Information

The supporting information includes specific details on the solution composition for each pH (Table S1) and a comparison of the FTIR spectra of the 1st and 2nd generations of the HTI's TFC membrane (Fig. S1).

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