Mixed Draw Solutions for Improved Forward Osmosis Performance

Ryan W. Holloway¹, Rudy Maltos², Johan Vanneste¹, and Tzahi Y. Cath^{1*}

¹Colorado School of Mines, Golden, Colorado, USA

²University of California, Merced, Merced, California, USA

* Corresponding author: e-mail: tcath@mines.edu; phone: (303) 273-3402; fax: (303) 273-3413

A manuscript prepared for possible publication in
Journal of Membrane Science

April 2015

Abstract

Reverse salt flux (RSF) of ions from the draw solution (DS) to the feed is a major drawback of forward osmosis (FO). RSF is reduced when divalent ion salts such as MgCl_2 and MgSO_4 that have larger hydrated radius are used instead of salts with monovalent ions only (e.g., NaCl). However, using divalent ion DSs comes with a cost – namely lower water flux compared to NaCl DS at similar osmotic pressures. The objective of this study was to enhance FO by lowering RSF while maintaining high water flux by adding low concentrations of divalent ions or organic ions to NaCl DS. We have demonstrated that water flux was similar for pure NaCl DS and mixed salts DS having low concentrations of divalent or organic ions at the same osmotic pressure of pure NaCl DS. Simultaneously, the average RSF was lower for all mixed salts DSs tested compared to pure NaCl DS. Results from a student t-test comparing the average RSF of the mixed salts DSs to the pure NaCl DS revealed that although the average RSF was lower for all the mixed DSs tested, only the mixed salts DS containing MgCl_2 has RSF significantly lower than the pure NaCl DS.

Keywords: Forward osmosis; reverse salt flux; desalination; draw solution; solute diffusion

1. Introduction

Osmosis or forward osmosis (FO) is a membrane separation technology that utilizes highly selective semipermeable membranes to extract water from a feed stream to a highly concentrated draw solution (DS) [1-4]. The driving force for mass transport in FO is the osmotic pressure difference between the low salinity feed and high salinity DS. The distinct advantage of FO over reverse osmosis (RO) and nanofiltration (NF) is that the system is operated at low hydraulic pressures, which reduces the fouling tendency of FO, even when treating impaired streams with very high fouling potential [5-9]. FO has been tested at bench-, pilot-, and full-scale for treatment of different impaired streams including municipal wastewater effluents [7], activated sludge [6, 10-13], digester centrate [9], and produced water from oil and gas exploration [5, 8].

The semipermeable membranes used in FO, typically cellulose triacetate (CTA) or thin film composite (TFC) polyamide membranes, allow water to diffuse across the membrane from the feed to the DS relatively freely while retaining most dissolved ions and organic compounds [7, 14-18]. Although FO membranes limit the diffusion of ions, solutes still diffuse at a slow rate through the membrane from the DS to the feed due to the high concentration difference of ions between the two streams. This phenomenon is known as reverse solute flux (RSF) [15, 19-22], and is undesired in FO applications because salt accumulation in the feed stream reduces the driving force for water flux (osmotic pressure difference), increases the cost of operation, and requires that the DS solutes be continuously replenished in closed-loop DS applications [10, 11, 23-25].

The rate at which solutes diffuse across a semipermeable membrane is a function of the salt permeability (B) and thickness (t) of the membrane active layer, the porosity (ε) and tortuosity (τ) of the membrane support layer, the concentration difference between the feed ($C_{F,b}$) and DS ($C_{D,b}$), and the diffusivity coefficient (D) of the solutes in solution [26]. Yip et al. [27] derived the RSF (J_s) equation (Equation 1) as a function of these parameters including the feed side boundary layer mass transfer coefficient (k):

$$J_s = B \left\{ \frac{C_{D,b} \exp\left(-\frac{J_w}{k}\right) - C_{F,b} \exp\left(\frac{J_w S}{D}\right)}{1 + \frac{B}{J_w} \left[\exp\left(\frac{J_w S}{D}\right) - \exp\left(-\frac{J_w}{k}\right) \right]} \right\} \quad (1)$$

where J_w is the forward water flux through the membrane and S is the structural parameter of the membranes porous support layer ($S = t \cdot \tau / \varepsilon$), where t , τ , and ε are the thickness, tortuosity, and porosity of the membrane support layer, respectively. As defined by Equation (1), the rate at which an ion diffuses through the selective active layer of a semi-permeable membrane depends on the solute selectivity of the active layer and chemical-physical properties of the solute. In general, diffusivity decreases with increasing molecular weight, charge, and hydrated radius of the ion [28]. The physical structure of the support layer also affects the rate of solute diffusion from the bulk DS to the active layer. Membranes that have a support layer with low porosity and high tortuosity experience higher internal concentration polarization (ICP), which is the dilution of the DS in the support layer and reduces the driving force for water flux [26]. The detrimental effect of ICP on water flux in FO is further exacerbated when solutes with low diffusivities such as magnesium, calcium, sulfate, and certain organic salts are used in the DS. Thus, the RSF can be favorably lower and the water flux unfavorably lower when using inorganic and organic DSs such as magnesium chloride (MgCl_2), magnesium sulfate (MgSO_4), and trisodium citrate compared to sodium chloride (NaCl) at the same osmotic pressures because of the lower diffusivity of the divalent and organic salts through the membrane active and support layers [15, 23, 24].

An ideal DS produces high water fluxes like those induced by NaCl and low RSFs like those observed when divalent inorganic and organic salts are used at common DS concentrations. Results described by Coday et al. [19] may provide insight into the potential of using DSs containing a mix of NaCl and divalent salts to take advantage of the high water flux associated with NaCl and low RSF associated with divalent DSs. It was demonstrated in their study that when synthetic seawater with low concentrations of divalent ions was used as a DS, the RSF of sodium across CTA and TFC membranes was reduced by 55% and 22%, respectively, and the RSF of chloride reduced by 25% and 27%, respectively, compared to DS containing only NaCl . Intriguingly, the water flux was equal for both draw solutions in experiments conducted with the TFC membrane and only slightly declined with the CTA membrane when seawater (a mixture of salts) DS was used instead of NaCl DS.

The reason for the reduced RSF and relatively constant water flux using seawater as a DS compared to NaCl was not explained by Coday et al.; however, there have been several studies on coupled solute flux in FO [15, 20, 21, 25] and preliminary modeling on the hindered transport

of monovalent ions for mixed salt solutions [29] that provide insight into the mechanisms behind these results. Hancock et al. [15, 20] and Phillip et al. [25] examined the coupled transport of ions across FO membranes between the feed stream and the concentrated DS using an array of solutes in each stream. The findings from these studies demonstrated that negatively and positively charged ions diffuse through the membrane at equal molar rates (or equivalents for divalent salts coupled with monovalent salts) to maintain electroneutrality in the system. Although both Hancock et al. [20] and Phillip et al. [25] concluded that the driving force for ion transport is governed by solution diffusion mechanisms and not electrostatic interactions (such as Donnan potential or ion exchange), their publications established that the transport of oppositely charged ions is affected by the diffusivity and mobility of the counter ion. For example, the more diffusive chloride ion essentially “drags” the less diffusive sodium ion across the membrane from the DS to the feed to maintain the electroneutrality in the system [25]. Conversely, magnesium in solution with chloride limits the transport of chloride across the membrane because magnesium has a much lower diffusivity compared to sodium or chloride in the membrane, thereby retarding the diffusion of chloride across the membrane to maintain electroneutrality. Recent studies have also shown that sodium and chloride diffuse across the membrane but transport of individual ions of certain charge is higher due to attraction to charged functional groups on the FO membrane active layer. It was demonstrated by Lu et al. [30] that the RSF of cations increased with increasing membrane electronegativity. Although membrane charge is not the primary focus of this study, it is important to understand that diffusion across FO membranes is not only a function of the charge of the ions in solution but the membrane used for separation.

In a transport modeling effort, Yaroshchuk et al. [29] included electrostatic interactions to the solution-diffusion model to determine if the diffusion of small monovalent ions would be hindered in the presence of divalent ions that are well rejected by the membrane. Results from the modeling effort illustrated that solute flux of sodium and chloride could be hindered in the presence of minor concentrations of divalent ions due to spontaneously arising electric fields. These fields form as a result of a charge imbalance that occurs as the more diffusive monovalent ions diffuse across the membrane at a higher rate than the well-rejected divalent ions. However, it must be noted that this model was tailored for NF membranes that have a lower selectivity to sodium and chloride than to divalent ions, as opposed to FO membranes that exhibit high

rejection of both monovalent and divalent ions. The difference in membrane selectivity to ions of different molecular size and charge is necessary for an electrical potential (Donnan potential) to develop that hinders the transport of ions through the membrane, which otherwise will freely diffuse. Thus, Donnan effects may not play an important role in ion mobility when highly selective FO membranes are used for separation. Other effects that must be considered as potential reasons for changes in sodium and chloride reverse flux in the presence of divalent ions have been described in the NF literature. These include adsorption of divalent cations to negatively charged polymeric membranes and charge shielding of the membrane due to the adsorption of the cations [31].

Though the mechanism for reduced sodium and chloride flux is complicated by ion–ion interactions and ion–membrane interactions, there is compelling empirical evidence presented in previous studies [19] that the diffusion of chloride and sodium are hindered when NaCl DS is mixed with minor concentrations of divalent ions. Thus, the main objective of the current study was to methodically determine the flux reduction of sodium and chloride through FO membranes while maintaining high FO process performance (high water flux) when small amounts of divalent inorganic and organic ions are added to an NaCl DS.

2. Material and methods

A series of bench-scale experiments were conducted to evaluate the water flux and RSF in FO when using DSs containing a mix of NaCl as the major solute and MgCl_2 , MgSO_4 , sodium acetate (NaACE), or trisodium citrate (NaCIT) as the minor solute. All mixed salts DS experiments were conducted at osmotic pressures equivalent to 0.5 M NaCl (23 bar) and 1 M NaCl (48 bar). Single salts (NaCl, MgCl_2 , MgSO_4 , sodium acetate, and trisodium citrate) were also tested as DSs at an osmotic pressure of 23 bar to compare the water flux and RSF of single salts to that of the mixed salts DSs.

2.1. Bench-scale apparatus

Single and mixed salts DS experiments were conducted under the same hydraulic conditions and at a constant DS concentration using an automated bench-scale apparatus. The apparatus is

comprised of a 4-L feed reservoir and a 4-L DS reservoir, two variable speed gear pumps (Cole-Parmer, Vernon Hills, IL), feed and DS flow meters, feed and DS heat exchangers, a chiller (Fisher Scientific, Waltham, MA), a cross-flow membrane cell, concentrated DS dosing pump (Anko, Bradenton, FL), an online DS conductivity probe (Cole-Parmer, Vernon Hills, IL), and an analytical balance (Denver Instrument, Bohemia, NY). The feed reservoir was placed on the analytical balance to measure changes in water weight as water diffused across the membrane from the feed to the DS. The recorded weight and membrane area (138 cm²) were used to calculate the water flux. A detailed schematic drawing of the bench-scale apparatus is shown in Fig. 1.

Fig. 1. Schematic drawing of the bench-scale apparatus used for single and mixed salts DS experiments. Adapted from [32].

The DS was continuously mixed using a magnetic stir bar and was maintained at a constant concentration using a peristaltic pump that dosed a doubly concentrated DS into the DS reservoir based on changes in the DS conductivity. The dosing pump was controlled using readings from the online conductivity probe connected to a programmable logic controller (UE9-Pro, LabJack Corp., Lakewood, CO) and a data acquisition and instrument control software (LabVIEW, National Instruments Corp., Austin, TX).

The feed and DS were continuously recirculated through the cross-flow FO membrane cell at a flow rate of 2 L/min and 1.2 L/min, respectively, and pressures of 6 psi and 4 psi, respectively.

The feed flow rate was selected to maintain a cross-flow velocity of 0.25 m/s in the feed channel per the standard methods for bench-scale FO testing [32]. The DS flow rate was set to maintain a slightly lower pressure (1-2 psi) in the DS channel than the feed to ensure that the FO membrane was not pushed into the spacer-free feed channel.

2.1.1. *Experimental procedure*

At the beginning of each experiment the feed reservoir was filled with 3 L of deionized water and the DS reservoir was filled with 1 L of premixed DS. The feed solution was dosed with 100 mg of ACS grade NaCl (approximately 33 mg/L) to guarantee that all feed samples were well within the detection limit of the analytical instruments used to measure individual ion concentrations in the feed and DS. The pH of the DS was adjusted to 7 using hydrochloric acid (HCl) or sodium hydroxide (NaOH) prior to each experiment. The pH of the DS was measured periodically during testing and adjusted as necessary to maintain it at 7. The pH of the deionized water feed was measured before and after each DS experiment. The bench-scale system was operated for 30 min with the feed and DS continuously recirculated through the symmetric cross-flow membrane cell and heat exchangers to ensure that the system was operating at constant water flux and temperature (20 °C) before the first samples were collected from the feed and DS reservoirs for analysis. The reservoirs were sampled again at the end of each experiment (90 minutes after the first sample); thus, each experiment was conducted for a total of 2 hrs.

Water flux was measured during all mixed salts DS experiments with DSs having osmotic pressures of 23 bar or 48 bar while water flux during single salt experiments, excluding NaCl, was only measured with DS having an osmotic pressure of 23 bar. The water flux for single salt DSs was not measured with DS having an osmotic pressure of 48 bar because the concentration of MgSO_4 needed for the DS dosing solution (431 g/L) exceeded the solubility limit (255 g/L) under the experimental conditions, and because of the high viscosity and difficulty to dissolve some of the other salts tested. The NaCl and mixed salts DS experiments were repeated four times with different membrane coupons to validate the accuracy of the results. The integrity of the membrane was assessed at the beginning of each experiment using an NaCl DS to confirm that the water flux and RSF were in a reasonable range for the TFC membrane used for testing. Experiments were conducted only once at the osmotic pressure of 23 bar to evaluate if trends in

mixed salts DS performance were similar to those observed for tests conducted at the higher osmotic pressure.

2.1.2. Draw solution chemistry

All experiments were conducted with ACS grade single salts (NaCl , $\text{MgCl}_2(\text{H}_2\text{O})_6$, $\text{MgSO}_4(\text{H}_2\text{O})_7$, sodium acetate trihydrate, and trisodium citrate dihydrate) and mixed salts DSs using NaCl as the major solute and MgCl_2 , MgSO_4 , sodium acetate, or trisodium citrate as minor solutes. The concentration of single salt DSs (MgCl_2 , MgSO_4 , sodium acetate, and trisodium citrate) used for testing was determined based on the equivalent osmotic pressure of a 0.5 M NaCl solution (23 bar). The osmotic pressure was calculated using OLI aqueous solution software (OLI, Cedar Knolls, NJ). Mixed salts DS experiments were evaluated at osmotic pressures equivalent to 0.5 M NaCl and 1.0 M NaCl (48 bar). For each osmotic pressure, the minor solute was added to an NaCl DS at concentrations equivalent to 5% and 10% of the total osmotic pressure. The concentration of each salt tested for the single salt and mixed salts DSs are summarized in Tables 1 and 2, respectively.

An additional experiment with MgCl_2 DS over a full-range of mixed salts DS concentrations was conducted to evaluate the reverse flux of magnesium, sodium, and chloride at increasing concentrations of MgCl_2 . The experiments were conducted at DS osmotic pressures equivalents of 23 bar and 48 bar; MgCl_2 was added to the NaCl DS at concentrations equivalent to 5%, 10%, 25%, 50%, 75%, and 100% of the total osmotic pressure. The concentrations of the salts used for the MgCl_2 experiment are summarized in Table 3.

Table 1. Concentration of salts in the DS during single solute DS experiments

DS osmotic pressure = 23 bar	
Solute	Solute conc., g/L
NaCl	29.2
MgCl_2	28.1
MgSO_4	107.8
Sodium acetate	69.9
Trisodium citrate	87.3
DS osmotic pressure = 48 bar	
Solute	Solute conc., g/L
NaCl	58.4

Table 2. Concentration of salts in the DS during mixed salts DS experiments

DS osmotic pressure = 23 bar			
Minor solute = 5% of total osmotic pressure (NaCl conc. = 27.9 g/L)		Minor solute = 10% of total osmotic pressure (NaCl concentration = 26.5 g/L)	
Minor solute	Minor solute conc., g/L	Minor solute	Minor solute conc., g/L
MgCl ₂	1.7	MgCl ₂	3.4
MgSO ₄	5.7	MgSO ₄	11.8
Sodium acetate	3.1	Sodium acetate	6.3
Sodium citrate	3.1	Sodium citrate	6.2
DS osmotic pressure = 48 bar			
Minor solute = 5% of total osmotic pressure (NaCl conc. = 55.7 g/L)		Minor solute = 10% of total osmotic pressure (NaCl concentration = 52.9 g/L)	
Minor solute	Minor solute conc., g/L	Minor solute	Minor solute conc., g/L
MgCl ₂	3.4	MgCl ₂	6.9
MgSO ₄	10.9	MgSO ₄	22.6
Sodium acetate	6.2	Sodium acetate	12.7
Sodium citrate	6.2	Sodium citrate	12.4

Table 3. Concentration of salts used during MgCl₂ mixed salts DS experiments evaluated over the full-range of MgCl₂ concentrations.

DS osmotic pressure = 23 bar		
Osmotic pressure of minor solute, %	MgCl ₂ , g/L	NaCl, g/L
5	1.7	27.9
10	3.4	26.5
25	7.4	21.9
50	15.5	14.6
75	21.6	7.3
100	28.1	0
DS osmotic pressure = 48 bar		
Osmotic pressure of minor solute, %	MgCl ₂ , g/L	NaCl, g/L
5	3.4	55.7
10	6.9	52.9
25	14.8	43.8
50	31.0	29.2
75	43.1	14.6
100	56.2	0

2.2. FO membranes

A TFC polyamide FO membrane from Hydration Technology Innovations (HTI, Albany, OR) was used for all experiments, and was installed with the active layer of the membrane facing the feed solution. The TFC membrane is relatively new to the FO membrane industry but has demonstrated to have higher solute selectivity and water permeability compared to the CTA membrane commonly used in FO applications [33].

2.3. Analytical procedures

Feed and DS samples collected during the experiments were analyzed for anions using ion chromatography (IC) (DC80, Dionex, Sunnyvale, CA) and for cations using an inductively coupled plasma (ICP) spectroscopy (Optima 3000, Perkin Elmer, Norwalk, CT). Feed and DS samples from experiments conducted with organic salts (sodium citrate and sodium acetate) were analyzed for total organic carbon (TOC) concentrations using a carbon analyzer (Sievers, GE Analytical Instruments, Boulder, CO). Except for the sulfate concentration in the deionized water feed that was near or below the detection limit (1 mg/L) of the ion chromatograph, the measured concentrations of all other cations, anions, and organic ions of concern in the feed and DS samples were above the lower detection limit and below the upper detection limit of the instruments used in this study.

3. Results and discussion

Mixed and single salt DSs were evaluated for general trends in water flux and RSF as well as statistical differences in the average RSF and specific reverse salt flux (ratio between reverse salt flux and forward water flux). Results were further evaluated to elucidate if the mechanisms controlling RSF (i.e., solution diffusion, coupled transport to support electroneutrality, and electrostatic interactions) adequately describe the observed differences in RSF for mixed salts DSs and NaCl DS.

3.1. Water flux

Water flux as a function of DS composition for single and mixed salts DS experiments conducted with DS osmotic pressures of 48 bar and 23 bar are shown in Fig. 2. The average water flux for the mixed salts DSs was very similar to the average water flux for the NaCl only DS (dashed line) for all experiments conducted at 48 bar osmotic pressure equivalent, except for 5% MgSO₄ and 10% MgSO₄, which had a slightly lower average water flux than that of the other tested DSs. However, the standard error (standard deviation divided by the square root of n samples) of water flux for the MgSO₄ mixed salts DSs was well within the standard error of all

DSs tested. The relatively high standard error in water flux for all DSs evaluated at 48 bar is very likely due to variation between different TFC membrane coupons. The difference in the performance between membrane coupons is evident as the water flux was within 10% for all DSs tested on an individual coupon while water flux varied by as much as 30% under the same operating conditions and DS concentrations between different coupons.

Fig. 2. Water flux for single and mixed salts DS experiments conducted with DS having (a) 48 bar ($n = 4$) and (b) 23 bar ($n = 1$) osmotic pressure. Standard error bars are included in (a).

Similar to experiments conducted with DSs having an osmotic pressure of 48 bar, the water flux for all mixed salts DSs evaluated at an osmotic pressure of 23 bar was nearly identical to the

water flux of the NaCl only DS (dashed red line). However, the water flux for three single salts (MgCl₂, MgSO₄, and trisodium citrate) was substantially lower than that of the NaCl DS at the same osmotic pressure. Similar results have been obtained by Achilli et al. [24] and Hancock et al. [15] testing single salts, and can be explained by the modified water flux (J_w) equations derived by Yip et al. [27], which includes the effect of internal ICP:

$$J_w = A \left\{ \frac{\pi_{D,b} \exp\left(-\frac{J_w}{k}\right) - \pi_{F,b} \exp\left(\frac{J_w S}{D}\right)}{1 + \frac{B}{J_w} \left[\exp\left(\frac{J_w S}{D}\right) - \exp\left(-\frac{J_w}{k}\right) \right]} \right\} \quad (2)$$

where A is the water permeability coefficient of the membrane, $\pi_{D,b}$ is the osmotic pressure of the bulk DS, $\pi_{F,b}$ is the osmotic pressure of the feed, and k is the feed side boundary layer mass transfer coefficient. Given that the same TFC membrane coupon and bulk DS osmotic pressure were used, all variables in Equation 2 are the same for each DS experiment except for the solute diffusion coefficient (D) and the solute permeability (B). The D values (calculated with OLI) for the single salt DSs tested are 1.6×10^{-5} , 1.1×10^{-5} , 0.9×10^{-5} , 1.2×10^{-5} , and 0.7×10^{-5} cm²/s for NaCl, MgCl₂, MgSO₄, sodium acetate, and trisodium citrate, respectively [28, 34]. The trend in the observed water flux for the single salt DSs closely follows that of the diffusion coefficient for each solute, with MgSO₄ and trisodium citrate having the lowest water flux and smallest diffusion coefficients and NaCl and sodium acetate having the highest water flux and diffusion coefficients. To further illustrate the trend in increasing water flux with increasing diffusion coefficient of the DS solute, water flux and the diffusion coefficient of each pure DS tested are shown in Fig. 3.

Fig. 3. Water flux and calculated diffusion coefficients for single salt DSs tested at an osmotic pressure of 23 bar.

The lower measured water flux of the single salts compared to NaCl is not unexpected; however, it is interesting that the water flux did not change for the mixed salts DS experiments conducted at DS osmotic pressures of 48 bar and 23 bar compared to pure NaCl DS. There is limited data in the literature for the diffusion of mixed electrolyte solutions except for NaCl and MgCl₂ for which there have been several studies on the diffusivity of these solutes at various mixed molar concentrations [35, 36]. Mathews et al. [35] demonstrated that the diffusivity for NaCl decreased at increasing molar concentration in a mixed electrolyte solution in which MgCl₂ was the major solute. However, for a mixed electrolyte solution with NaCl as the major salt and MgCl₂ as the minor salt, the diffusivity for NaCl was virtually constant and the diffusivity for MgCl₂ decreased with increasing molar concentration [36]. Because the diffusivity of NaCl is similar in the mixed and NaCl only DS experiments, the effect of ICP in the porous support layer and the measured water flux for all mixed salts DSs is very similar to the NaCl DS at the same osmotic pressure.

3.2. Reverse and specific reverse salt flux

The RSF of all evaluated single salt and mixed salts DSs having an osmotic pressure of 48 bar were repeated four times with a different coupon for each test and experiments with DSs

1
2
3
4 having an osmotic pressure of 23 bar were conducted only once. The total RSF of all major ions
5 diffusing from the DS to the feed was calculated on a molar basis for DS experiments conducted
6 with DSs having osmotic pressures of 48 bar and 23 bar, and are shown in Fig. 4.
7
8

9
10 The average total RSF for all evaluated single and mixed salts DSs was less than that of the
11 NaCl DS at the same DS osmotic pressure. In general, the average total RSF for mixed salts DSs
12 tested at 10% of the total osmotic pressure was lower than the RSF of the 5% mixtures except for
13 MgSO_4 at DS total osmotic pressures of 23 bar and 48 bar and sodium acetate at DS a total
14 osmotic pressure of 23 bar. The RSF for the mixed DSs tested with a DS having an osmotic
15 pressure of 23 bar are somewhat inconsistent—illustrated by the fact that some mixed salts DSs
16 tested at 5% of the total osmotic pressure exhibited lower RSF than the same mixed salts DSs
17 evaluated at 10% of the total osmotic pressure. Although there were a few observations that were
18 outside the general trend; overall, it appears that the mixed salts DSs did reduce the RSF
19 compared to a pure NaCl DS.
20
21
22
23
24
25
26
27

28 The variability (wide standard error) in RSF data for the experiments conducted at an
29 osmotic pressure of 48 bar may be attributed to the relatively small sample size ($n = 4$) as well as
30 differences in the physical and chemical properties of the four TFC membrane coupons tested.
31 Although it is difficult to draw conclusions from small sample sets ($n < 20$), a student t-test was
32 conducted between the average total RSF of each group of mixed salts DSs (MgCl_2 , MgSO_4 ,
33 sodium acetate, and trisodium citrate) at 5% and 10% of the total osmotic pressure and the
34 average total RSF of an NaCl DS with an alpha level equal to 0.05. The student t-test was only
35 conducted for experimental results obtained with a DS having an osmotic pressure of 48 bar
36 because there are multiple results ($n = 4$) that can be used to compute the p-values. There was a
37 significant difference ($p = 0.02$) between the mean RSF of 10% MgCl_2 and NaCl DSs. There was
38 no statistical significant difference between $p = 0.17$ (5% MgSO_4) and $p = 0.51$ (5% sodium
39 acetate) for the other mixed salts DSs compared to NaCl. However, of the 40 mixed salts DS
40 experiments conducted with DSs having an osmotic pressure of 48 bar and 23 bar, there were
41 only two occasions (5% MgSO_4 and 5% sodium acetate at an osmotic pressure of 48 bar) in
42 which the measured RSF was higher for a mixed salts DS compared to a DS containing only
43 NaCl, indicating that there was a positive effect (lower RSF) using the mixed salts DSs
44 compared to NaCl.
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

Fig. 4. Total RSF for single salt and mixed salts DS experiments conducted with DS having osmotic pressures of (a) 48 bar ($n = 4$) and (b) 23 bar ($n = 1$). The calculated RSF included all inorganic ions (measured with IC and ICP) and all organic compounds (measured using a TOC analyzer) that diffused from the DS to the feed.

Although the standard error for the water flux and RSF is relatively high for experiments conducted with DS having osmotic pressure of 48 bar, the initial results from both mixed salts DS experiments conducted at 48 bar and 23 bar osmotic pressure illustrate that the water flux is maintained and the RSF can be reduced when using NaCl DSs mixed with ions with lower diffusivities. A common way to evaluate the performance of DSs in FO is to calculate the specific RSF (J_s/J_w), defined as the RSF (J_s) normalized by the forward water flux (J_w). The

specific RSF is an informative FO parameter because it provides a quantitative measure of the mass of solutes lost from the DS per volume of water recovered from the feed. The specific RSF for the mixed salts DSs having osmotic pressures of 48 bar and 23 bar are illustrated in Fig. 5. The specific RSF for the single salt DSs experiments are also shown in Fig. 5.

Fig. 5. Specific RSF (J_s/J_w) for mixed salts DS experiments conducted with DS having osmotic pressures of (a) 48 bar ($n = 4$) and (b) at 23 bar ($n = 1$). Solute flux includes all inorganic ions and organic compounds that diffused from the DS to feed for each single and mixed salts DS experiment.

Similar to the water flux and RSF results, the average specific RSF for all mixed salts DSs and single salt experiments was lower than that of the NaCl DS at similar DS osmotic pressure.

Additionally, the average specific RSF decreased between mixed salts DS experiments with the minor solute contributing up to 5% and 10% of the total osmotic pressure with the only exception being for 5% and 10% MgSO_4 and 5% and 10% sodium acetate for experiments conducted with a DS having an osmotic pressure of 23 bar. The lowest specific RSF was observed for the single salt DSs due to the low diffusivity of the divalent ions and organic salts in solution. Specific RSF had the lowest value for the single salt test evaluated with MgSO_4 because both magnesium and sulfate diffuse slowly through the membrane due to the large molecular and hydrated sizes and charge of both divalent ions.

A student t-test was conducted for the mixed salts DSs and NaCl only DS conducted at an osmotic pressure of 48 bar to evaluate if there was a significant difference between the average specific RSF for each mixed salts DS compared to NaCl (α level = 0.05). Similar to the RSF results, there was a statistically significant difference between NaCl and 10% MgCl_2 ($p = 0.04$). There was not a statistically significant difference between the average specific RSF for all other evaluated mixed salts DSs compared to NaCl. It is intriguing that the addition of MgCl_2 as a small contribution to the total osmotic pressure is the only minor solute tested that has a significant effect on the total average RSF and specific RSF. There are only two very simple reasons that the total RSF is lower for the mixed MgCl_2 experiments compared to the other mixed salts DSs tested. First, the reverse sodium and chloride flux was the same for all mixed salts DSs, but RSF of the minor ions was greater for the mixed salts DSs not containing MgCl_2 ; thereby, increasing the total RSF. Second, reverse sodium and chloride flux was reduced to a greater extent with the addition of MgCl_2 to the NaCl DS compared to the other mixed salts DSs tested. To elucidate if there was a larger contribution of minor solutes to the total RSF for the mixed salts DSs containing MgSO_4 , sodium acetate, and trisodium citrate compared to MgCl_2 , the average RSF for the individual multivalent ions and organic compounds tested in the mixed salts DS experiments were calculated and are summarized in Table 4.

Table 4. Average RSF of individual multivalent ions and organic compounds for mixed salts DS experiments conducted with DS osmotic pressure of 48 bar. The standard error for each average RSF is also provided.

	MgCl_2	MgSO_4		Sodium acetate	Sodium citrate
Percent osmotic pressure	Mg^{2+} flux, mmol/m ² -hr	Mg^{2+} flux, mmol/m ² -hr	SO_4^{2-} flux, mmol/m ² -hr	Acetate flux, mmol/m ² -hr	Citrate flux, mmol/m ² -hr
5%	0.08 ± 0.10	0.06 ± 0.02	0.01 ± 0.01	0.53 ± 0.31	0.31 ± 0.15
10%	0.11 ± 0.02	0.13 ± 0.05	0.02 ± 0.01	0.71 ± 1.88	0.75 ± 0.35

The RSF for the individual multivalent ions and organic compounds tested was similar for all mixed salts DSs and provided very little to the total RSF. On average, the RSF of the minor ions (Mg^{2+} , SO_4^{2-} , acetate, and citrate) contributed less than 1% to the total RSF. Therefore, any substantial reductions in RSF with the addition of MgCl_2 to the majority NaCl DS was due to changes in the sodium and chloride reverse flux. The sodium and chloride flux for the NaCl only DS and mixed salts DSs having an osmotic pressure of 48 bar are shown in Fig. 6.

Fig. 6. Sodium and chloride reverse flux for mixed salts DS and NaCl only DS experiments conducted with the DS having an osmotic pressure of 48 bar.

The average sodium and chloride flux was lowest ($<25 \text{ mmol/m}^2\text{-hr}$) for the experiment conducted with MgCl_2 making up 10% of the osmotic pressure, considerably lower than the sodium and chloride reverse flux for the NaCl only DS (sodium flux $>35 \text{ mmol/m}^2\text{-hr}$ and chloride flux $>30 \text{ mmol/m}^2\text{-hr}$). The average sodium flux was noticeably higher than the average chloride flux for the experiments conducted with the pure NaCl DS. Other researchers have also noted higher sodium flux than chloride flux when investigating transport across TFC membranes [19]. This difference has been associated with the positively charged sodium ion being attracted to the negatively charged carboxyl groups on the active layer of the TFC membrane. In studies that have observed sodium diffusing across the membrane at a higher rate than chloride, ion electroneutrality has been shown to be maintained by the coupled diffusion of sodium with

another positively charged ion diffusing in the opposite direction [30]. In the current study, electroneutrality was likely maintained by the coupled diffusion of H^+ from the feed to the DS as sodium diffused from the DS to the feed. In general, the pH of the feed increased by 0.5 for each single salt and mixed salts DS tested, indicating that H^+ very likely diffused from the feed to the DS. Although the rate of sodium flux across the membrane was likely higher than chloride, in the current study no statistically significant difference could be calculated for the data presented in Fig. 6, and therefore will be described as diffusing across the membrane at approximately equal molar ratios.

As discussed above, Hancock et al. [15] and Phillip et al. [25] demonstrated that although chloride has a higher diffusivity than sodium, these two counter ions diffuse across the membrane at equal molar ratios to maintain the electroneutrality of the system. Thus, the more diffusive chloride ion crosses the membrane and essentially “drags” the sodium ion along, thereby maintaining electroneutrality. Because sodium and chloride diffuse across the membrane at equal molar ratios, there must be a mechanism in which $MgCl_2$ in solution with NaCl hinders the diffusion of sodium or chloride to reduce the reverse flux of these two counter ions.

Though electroneutrality has been used to explain the diffusion of sodium and chloride at equal molar ratios, it has been hypothesized that the diffusion of solutes across the membrane is not driven by a difference in electrical potential (such as Donnan effects) across the membrane, but exclusively governed by solution-diffusion mechanisms in which ions diffuse across the membrane as a function of the concentration gradient of the individual ions between the DS and the feed [20]. This hypothesis appears to be valid in systems containing only two ions in the DS, as was tested by Hancock et al. [15] and Phillip et al. [25]; but in the current study the concentration of chloride increased as more $MgCl_2$ was added to the NaCl DS and the concentration of sodium increased as more trisodium citrate was added to the NaCl DS. The lowest concentration of sodium and chloride in the DS was for the experiment conducted with 10% $MgSO_4$ when sodium and chloride were replaced with magnesium and sulfate at increasing $MgSO_4$ concentrations. If the diffusion of ions across the membrane were strictly governed by the concentration gradient, it would be expected that adding $MgSO_4$ would have the largest effect on reducing the reverse diffusion of sodium and chloride across the membrane; this was not the case in the current study.

From the reverse sodium and chloride flux results presented in Fig. 6 it is probable that sodium and chloride flux is limited by other mechanisms besides differences in concentration for mixed salts DSs. Therefore, there must be other interactions (such as electrostatic interactions, Hofmeister effects, and charge shielding) between individual ions or between ions and the membrane surface that have a significant impact on the transport of sodium and chloride across the membrane and lowering the average RSF. It may be that the lower mobility of magnesium compared to sodium and chloride hinder the diffusion of sodium and chloride as a result of electrostatic interactions or other phenomena such as differences in the diffusion coefficient for mixed electrolyte solutions [35, 36], Hofmeister effects [21, 37], or adsorption of magnesium to the membrane functional groups resulting in charge shielding and steric hindrance [31].

3.3. *Magnesium chloride reverse and specific reverse solute flux*

The mixed salts DSs containing MgCl_2 exhibited the lowest average RSF and specific RSF of all the DSs tested at a DS osmotic pressure of 48 bar. The mixed salts DS tested with 10% MgCl_2 with a DS having an osmotic pressure of 23 bar also performed well; although, the RSF was not as low as the mixed salts DSs tested with sodium citrate or single salt DSs (MgCl_2 , MgSO_4 , sodium acetate, and trisodium citrate) at the lower osmotic pressure. Based on the performance of MgCl_2 as a mixed salts DS, MgCl_2 was further evaluated for water flux and RSF over a range of mixed DS concentrations including 5%-OP (percent contribution of MgCl_2 to the total DS osmotic pressure), 10%-OP, 25%-OP, 50%-OP, 75%-OP, and 100%-OP of the total osmotic pressure. Water flux and RSF for MgCl_2 experiments conducted with a DS having osmotic pressures of 48 bar and 23 bar are presented in Fig. 7. It is important to note that only one experiment was conducted with a DS having osmotic pressures of 48 bar and 23 bar (Fig. 7) over the range of mixed DS concentrations to elucidate general trends in water flux and RSF over a range of mixed MgCl_2 concentrations.

Fig. 7. Water and total RSF (including Na^+ , Cl^- , Mg^{2+}) as a function of MgCl_2 contribution to the total osmotic pressure of DSs having osmotic pressures of (a) 48 bar ($n = 1$) and (b) 23 bar ($n = 1$).

For the mixed NaCl-MgCl_2 DS having total osmotic pressure of 48 bar, water flux decreased by 22% (from 13.4 to 10.5 $\text{L/m}^2\text{-hr}$) when transitioning from 100% NaCl DS (0% MgCl_2) to a 100% MgCl_2 DS (Fig. 7a), and water flux decreased by 16% (from 10.9 to 9.2 $\text{L/m}^2\text{-hr}$) for DSs having total osmotic pressure of 23 bar (Fig. 7b). Interestingly, the water flux declined by less than 6% for both mixed NaCl-MgCl_2 DS experiments between the pure NaCl DS and the 50%-OP MgCl_2 DS. Beyond 50%-OP MgCl_2 the water flux declined by approximately 17% and 10% for experiments conducted with DSs having a total osmotic pressure of 48 bar and 23 bar, respectively. The limited reduction in water flux at mixed NaCl-MgCl_2 less than 50%-OP MgCl_2 may be attributed to the higher diffusivity of the sodium and chloride ions at lower mixed MgCl_2 concentrations.

The change in RSF with increasing MgCl_2 concentrations was somewhat similar between total DS osmotic pressures of 48 bar and 23 bar. For MgCl_2 evaluated with a DS having an osmotic pressure of 23 bar, RSF decreased somewhat linearly from a 53.9 to 1.46 $\text{mmol/m}^2\text{-hr}$ between the pure NaCl and pure MgCl_2 (Fig. 7b). For mixed NaCl-MgCl_2 DS experiments having an osmotic pressure of 48 bar (Fig. 7a), the RSF decreased linearly from 85.3 $\text{mmol/m}^2\text{-hr}$ to 4.5 $\text{mmol/m}^2\text{-hr}$ across the full range of DS solute ratios tested. To more easily interpret the simultaneous water flux and RSF, specific RSF was calculated for MgCl_2 over the range of DS solute ratios tested at total DS osmotic pressures of 48 bar and 23 bar, as illustrated in Fig. 8.

Fig. 8. Specific RSF as a function of minor solute (MgCl₂) contribution to total osmotic pressure for DSs having total osmotic pressures of (a) 48 bar (n = 1) and (b) 23 bar (n = 1).

RSF decreased fairly linearly across the full-range of mixed salts DS at a total osmotic pressure of 48 bar, from 6.3 mmol/L (pure NaCl DS) to 0.43 mmol/L (pure MgCl₂ DS). For NaCl-MgCl₂ ratios evaluated at a total DS osmotic pressure of 23 bar, specific RSF initially declined by 15% with the addition of 5%-OP MgCl₂ and was constant up to 50%-OP MgCl₂, then specific RSF declined abruptly at 75%-OP MgCl₂ and 100% MgCl₂. The reason for the sharper decline in specific RSF once MgCl₂ became the major salt (75%-OP and 100% MgCl₂) and NaCl became the minor salt (25%-OP and 0% NaCl) at a total DS osmotic pressure of 23 bar may be a result of the lower diffusivity of NaCl with increasing molar concentrations of MgCl₂, as has been reported by Mathew et al. [35], or to a decreased driving force (concentration gradient) as sodium is replaced by magnesium at MgCl₂-OP ratios above 75%.

3.4. Transport mechanism

From the limited data set it is difficult to distill an encompassing theory that predicts interactions between different ions in solution and between ions and the membrane. However, a transport mechanism can be envisioned that provides an explanation for the reduction in solute flux while the water flux is unaffected or slightly increases at low mixed DS concentrations. It is hypothesized that the ion concentration inside the pore space of the active layer differs substantially from the bulk DS concentration, which would explain the limited non-linear

decrease in water flux with increasing minor ion concentration to a majority NaCl DS. If it is assumed that the RSF of individual ions is indicative of the concentration of the ion in the pore space, then the pore composition can be calculated using the measured RSF and compared to the bulk DS ion composition to determine if the composition in the active layer is more representative of a pure NaCl DS or a mixed salts DS. To elucidate the composition of the DS in the pore space compared to the bulk DS, the ratio of magnesium RSF to the total RSF was plotted against the ratio of magnesium to the total ion (sodium, chloride, and magnesium) concentration in the bulk DS as shown in Fig. 9.

Fig. 9. The ratio of magnesium RSF to total RSF as a function of draw solution composition for (a) 48 bar and (b) 23 bar DS osmotic pressures, respectively

The results presented in Fig. 9 confirm that there is ion partitioning in the pore space of the active layer of the membrane compared to the bulk DS. This supports the hypothesis that the observed non-linear decrease in water flux at increasing magnesium to total DS solute flux ratios may be in part due to non-linear increases in the magnesium pore space concentration at increasing magnesium to total DS solute flux ratios. Ion partitioning arises most likely for two reasons considering Equation 1. First, at low magnesium to total DS solute flux ratios the driving force for transport of the minor ion (magnesium) is much lower due to the very low concentration difference of magnesium between the DS and feed solution and hence, the RSF is much lower as well. As the ratio of magnesium to total DS solute flux ratio increases, the RSF of

magnesium also increases because of the greater difference in magnesium concentration between the DS and feed solution (Fig. 9). Second, the diffusivity of the different ions differs with the less diffusive being depleted in the pore space relative to the bulk DS. MgCl_2 has indeed a lower diffusivity than NaCl (Fig. 3.). Whether it is differences in concentration, diffusivity, or other mechanisms that are responsible for the ion partitioning in the membrane active layer, it is evident that the pore composition of the pore space increases non-linearly (Fig. 9) and may be responsible for the non-linear decrease in water flux (Fig. 7) at increasing magnesium to total DS solute flux ratios.

At this point the non-linear evolution of the pore concentration was identified as the basis for the non-linear decrease in water flux at increasing minor ion concentrations. A tentative graphical representation illustrated in Fig. 10 and an analysis of the forces at the pore level might further increase the understanding of the mechanisms at play and elucidate some peculiarities in the results, such as the slight increase in water flux at low minor ion concentrations. Unlike pressure driven membrane processes, in FO it can be expected that the resistance to water transport inside the membrane is not only governed by the membrane itself (A , S value in Equation 2) but also by the RSF, and hence the ion composition inside the pore space. This is also confirmed by Equation 2 that predicts a lower water flux with increased RSF (higher B value). Conversely, if the RSF is reduced without increasing resistance to water transport, the water flux should increase. Indeed, the water flux seems to be systematically higher for the mixed solutions at lower concentrations (Figs. 2 and 7).

Fig. 10. Illustration of potential water and ion transport in FO employing a pure NaCl, mixed salts, and MgCl₂ DS.

From Fig. 10 it can be envisioned that the ion partitioning in the pores of the membrane active layer will affect water and ion transport. In the case of a pure NaCl DS, sodium and chloride diffuse rapidly through the pore because of the high diffusivity and smaller hydrated radius of the ions; however, due to the smaller size of the ions in the pore, water traveling in the opposite direction of the ions is not restricted. For a pure MgCl₂ DS, chloride flux is limited to maintain electroneutrality with the slower diffusing magnesium ions; however, the large hydrated radius of magnesium limits water transport in the opposite direction because the pore is essentially blocked with magnesium ions. In the case of a mixed salts DS, the magnesium ions travel at a much lower velocity than sodium and chloride ions due to lower diffusivity and lower driving force, retarding the transport of NaCl because of steric hindrances, ion shielding, and electrostatic interactions. However, water molecules will experience no, or only a very slight increased, resistance to transport in the other direction compared to a pure MgCl₂ solution. As

such, the reverse sodium and chloride flux is reduced and water flux is maintained or slightly increased when small concentrations of slowly diffusing ions are added to a majority NaCl DS.

4. Conclusions

The results from this study demonstrate that addition of salts having divalent and organic ions at relatively low concentrations, and particularly MgCl_2 , to an NaCl DS can be effective in reducing RSF while maintaining high water flux. There was a positive effect (lower RSF) with all mixed salts DSs tested with DSs having an osmotic pressure of 48 bar and 23 bar but the mixed salts DS containing 10% MgCl_2 at an osmotic pressure equivalent to 48 bar was the only mixed salts DS that had a statistically significant lower RSF compared to a pure NaCl DS. This is not to state that the other mixed salts DSs are not effective; however, additional research would be required to determine statistical significance. The RSF was not only reduced when MgCl_2 was added to a majority NaCl DS but the water flux also increased slightly at the lowest concentrations of MgCl_2 added to an NaCl DS. It is hypothesized that the composition of the mixed salts DS in the pore space of the active layer of the membrane closely resembles that of a pure NaCl DS combined with very low concentrations of magnesium. Although there is a small amount of magnesium in the pore space, the low diffusivity of magnesium preventing sodium and chloride from diffusing through the pore at a high rate. It is also important to note that there is a low concentration of magnesium in the pore because it does not limit water from diffusing through the pore in the opposite direction of the RSF as is the case when high concentrations of MgCl_2 are used in the DS. This manuscript illustrates the potential for mixed DSs to enhance FO for closed loop operations by selecting the appropriate combination of solutes.

Acknowledgments

The authors would like to thank the National Science Foundation Engineering Research Center Program under Cooperative Agreement EEC-1028968 (ReNUWIt), the NSF REU program, and the US Department of Energy, Advanced Research Projects Agency-Energy (ARPA-e) Award #0670-3228 for supporting this study. The authors thank Hydration Technology Innovations, LLC for providing membranes for this research. The author would also like to thank Dr. Bryan Coday and to Mr. Tani Cath for their technical and scientific support.

References

- [1] T.Y. Cath, A.E. Childress, M. Elimelech, Forward osmosis: principles, applications, and recent developments, *J Membrane Sci* 281 (2006) 70-87.
- [2] C. Klaysom, T.Y. Cath, T. Depuydt, I.F.J. Vankelecom, Forward and pressure retarded osmosis: Potential solutions for global challenges in energy and water supply, *Chem Soc Rev* 42 (2013) 6959-6989.
- [3] S. Zhao, L. Zou, C.Y. Tang, D. Mulcahy, Recent developments in forward osmosis: opportunities and challenges, *J Membrane Sci* 396 (2012) 1-21.
- [4] T.-S. Chung, S. Zhang, K.Y. Wang, J. Su, M.M. Ling, Forward osmosis processes: yesterday, today and tomorrow, *Desalination* 287 (2012) 78-81.
- [5] B.D. Coday, P. Xu, E.G. Beaudry, J. Herron, K. Lampi, N.T. Hancock, T.Y. Cath, The sweet spot of forward osmosis: Treatment of produced water, drilling wastewater, and other complex and difficult liquid streams, *Desalination* 333 (2014) 23-35.
- [6] E.R. Cornelissen, D. Harmsen, K.F. de Korte, C.J. Ruiken, J.J. Qin, H. Oo, L.P. Wessels, Membrane fouling and process performance of forward osmosis membranes on activated sludge, *J Membrane Sci* 319 (2008) 158-168.
- [7] N.T. Hancock, P. Xu, M.J. Roby, J.D. Gomez, T.Y. Cath, Towards direct potable reuse with forward osmosis: Technical assessment of long-term process performance at the pilot scale, *J Membrane Sci* 445 (2013) 34-46.
- [8] K.L. Hickenbottom, N.T. Hancock, N.R. Hutchings, E.W. Appleton, E.G. Beaudry, P. Xu, T.Y. Cath, Forward osmosis treatment of drilling mud and fracturing wastewater from oil and gas operations, *Desalination* 312 (2013) 60-66.
- [9] R.W. Holloway, A.E. Childress, K.E. Dennett, T.Y. Cath, Forward osmosis for concentration of anaerobic digester centrate, *Water Res* 41 (2007) 4005-4014.
- [10] A. Achilli, T.Y. Cath, E.A. Marchand, A.E. Childress, The forward osmosis membrane bioreactor: A low fouling alternative to MBR processes, *Desalination* 239 (2009) 10-21.
- [11] R.W. Holloway, J. Regnery, L.D. Nghiem, T.Y. Cath, Removal of trace organic chemicals and performance of a novel hybrid ultrafiltration-osmotic membrane bioreactor, *Environ Sci Technol* 48 (2014) 10859-10868.
- [12] G. Qiu, Y.-P. Ting, Short-term fouling propensity and flux behavior in an osmotic membrane bioreactor for wastewater treatment, *Desalination* 332 (2014) 91-99.

- [13] X. Wang, Y. Chen, B. Yuan, X. Li, Y. Ren, Impacts of sludge retention time on sludge characteristics and membrane fouling in a submerged osmotic membrane bioreactor, *Bioresource Technol* 161 (2014) 340-347.
- [14] A.A. Alturki, J.A. McDonald, S.J. Khan, W.E. Price, L.D. Nghiem, M. Elimelech, Removal of trace organic contaminants by the forward osmosis process, *Sep Purif Technol* 103 (2013) 258-266.
- [15] N.T. Hancock, T.Y. Cath, Solute coupled diffusion in osmotically driven membrane processes, *Environ Sci Technol* 43 (2009) 6769-6775.
- [16] N.T. Hancock, P. Xu, D.M. Heil, C. Bellona, T.Y. Cath, Comprehensive bench- and pilot-scale investigation of trace organic compounds rejection by forward osmosis, *Environ Sci Technol* 45 (2011) 8483-8490.
- [17] X. Jin, J.H. Shan, C. Wang, J. Wei, C.Y.Y. Tang, Rejection of pharmaceuticals by forward osmosis membranes, *J Hazard Mater* 227 (2012) 55-61.
- [18] R.V. Linares, V. Yangali-Quintanilla, Z.Y. Li, G. Amy, Rejection of micropollutants by clean and fouled forward osmosis membrane, *Water Res* 45 (2011) 6737-6744.
- [19] B.D. Coday, D.M. Heil, P. Xu, T.Y. Cath, Effects of transmembrane hydraulic pressure on performance of forward osmosis membranes, *Environ Sci Technol* 47 (2013) 2386-2393.
- [20] N.T. Hancock, W.A. Phillip, M. Elimelech, T.Y. Cath, Bidirectional permeation of electrolytes in osmotically driven membrane processes, *Environ Sci Technol* 45 (2011) 10642-10651.
- [21] G.J. Irvine, S. Rajesh, M. Georgiadis, W.A. Phillip, Ion selective permeation through cellulose acetate membranes in forward osmosis, *Environ Sci Technol* 47 (2013) 13745-13753.
- [22] J.S. Yong, W.A. Phillip, M. Elimelech, Coupled reverse draw solute permeation and water flux in forward osmosis with neutral draw solutes, *J Membrane Sci* 392 (2012) 9-17.
- [23] K.S. Bowden, A. Achilli, A.E. Childress, Organic ionic salt draw solutions for osmotic membrane bioreactors, *Bioresource Technol* 122 (2012) 207-216.
- [24] A. Achilli, T.Y. Cath, A.E. Childress, Selection of inorganic-based draw solutions for forward osmosis applications, *J Membrane Sci* 364 (2010) 233-241.
- [25] W.A. Phillip, J.S. Yong, M. Elimelech, Reverse draw solute permeation in forward osmosis: Modeling and experiments, *Environ Sci Technol* 44 (2010) 5170-5176.

- [26] J.R. McCutcheon, M. Elimelech, Influence of concentrative and dilutive internal concentration polarization on flux behavior in forward osmosis, *J Membrane Sci* 284 (2006) 237-247.
- [27] N.Y. Yip, A. Tiraferri, W.A. Phillip, J.D. Schiffman, L.A. Hoover, Y.C. Kim, M. Elimelech, Thin-film composite pressure retarded osmosis membranes for sustainable power generation from salinity gradients, *Environ Sci Technol* 45 (2011) 4360-4369.
- [28] E.L. Cussler, Diffusion, mass transfer in fluid systems, Second Edition, Cambridge University Press, Cambridge Cambridgeshire ; New York, 1997, 052123171X.
- [29] A. Yaroshchuk, M.L. Bruening, E.E.L. Bernal, Solution-diffusion-electro-migration model and its uses for analysis of nanofiltration, pressure-retarded osmosis and forward osmosis in multi-ionic solutions, *J Membrane Sci* 447 (2013) 463-476.
- [30] X. Lu, C. Boo, J. Ma, M. Elimelech, Bidirectional diffusion of ammonium and sodium cations in forward osmosis: Role of membrane active layer surface chemistry and charge, *Environ Sci Technol* 48 (2014) 14369-14376.
- [31] J. Garcia-Aleman, J.M. Dickson, Permeation of mixed-salt solutions with commercial and pore-filled nanofiltration membranes: membrane charge inversion phenomena, *Journal of Membrane Science* 239 (2004) 163-172.
- [32] T.Y. Cath, M. Elimelech, J.R. McCutcheon, R.L. McGinnis, A. Achilli, D. Anastasio, A.R. Brady, A.E. Childress, I.V. Farr, N.T. Hancock, J. Lampi, L.D. Nghiem, M. Xie, N.Y. Yip, Standard methodology for evaluating membrane performance in osmotically driven membrane processes, *Desalination* 312 (2013) 31-38.
- [33] N.Y. Yip, A. Tiraferri, W.A. Phillip, J.D. Schiffman, M. Elimelech, High performance thin-film composite forward osmosis membrane, *Environ Sci Technol* 44 (2010) 3812-3818.
- [34] M.Z. Southard, L.J. Dias, K.J. Himmelstein, V.J. Stella, Experimental determinations of diffusion coefficients in dilute aqueous solution using the method of hydrodynamic stability, *Pharmaceut Res* 8 (1991) 1489-1494.
- [35] R. Mathew, J.G. Albright, D.G. Miller, J.A. Rard, Isothermal diffusion coefficients for sodium chloride-magnesium chloride-water at 25.degree.C. 4. Solute concentration ratio of 1:3, *J Phys Chem-Us* 94 (1990) 6875-6878.
- [36] R. Mathew, L. Paduano, J.G. Albright, D.G. Miller, J.A. Rard, Isothermal diffusion coefficients for sodium chloride-magnesium chloride-water at 25.degree.C. 3. Low magnesium chloride concentrations with a wide range of sodium chloride concentrations, *J Phys Chem-Us* 93 (1989) 4370-4374.

[37] W. Kunz, P. Lo Nostro, B.W. Ninham, The present state of affairs with Hoffmeister effects, Curr Opin Colloid In 9 (2004) 1-18.