Zeta potential of commercial RO membranes: influence of source water type and chemistry

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Abstract

Streaming potential measurements have typically been performed on reverse osmosis (RO) and nanofiltration (NF) membranes using simple solution chemistries that are representative of those found in natural waters and wastewaters. In this investigation, streaming potential measurements were performed on RO membranes using actual membrane feed waters. Tertiary wastewater effluent, which serves as membrane feedwater at the Orange County Water District (Fountain Valley, California) and river water from the Brazos River (Brazos, Texas) were used. Additionally, the effects of glutaraldehyde (a membrane storage agent) and atrazine (a pesticide) on membrane surface charge were evaluated. The pesticide was evaluated in the presence and absence of humic acid. Results showed a more positive zeta potential in the presence of the Brazos River water, most likely due to the presence of divalent cations (Ca$^{2+}$ and Mg$^{2+}$). For the tertiary wastewater effluent, adsorption of organic acids in the wastewater effluent may have been the cause of the more negative zeta potential in the low pH range and the presence of divalent cations may have been the cause of the more positive zeta potential in the high pH range. The glutaraldehyde and atrazine showed little effect on the surface charge of the membranes. However, atrazine in the presence of humic acid showed a significant effect on the zeta potential, causing the membrane to have a less negative surface charge than in the presence of the humic acid alone.

Keywords: Zeta potential; Streaming potential; Membrane charge; Reverse osmosis membrane

1. Introduction

Several works on streaming potential measurements of microfiltration (MF) (e.g., Kim et al. [1] and Lettmann et al. [2]), ultrafiltration (UF) (e.g., Nystrom et al. [3], Causserand et al. [4], Nystrom et al. [5], Rodemann and Staude [6], Kim et al. [1], Blank et al. [7], Mockel et al. [8], and Szymczyk et al. [9]), NF (e.g., Nystrom et al. [10], Childress and Elimelech [11], Blank et al. [7], Hagmeyer and Gimbel [12], Peeters et al.
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[13], Childress and Elimelech [14], and Ernst et al. [15]), and RO (e.g., Elimelech et al. [16], Childress and Elimelech [11], and Benavente and Jonsson [17]) membranes have appeared in the literature over the past decade. These works include investigations of both pore streaming potential (e.g., Nystrom et al. [3], Causserand et al. [4], Nystrom et al. [5], Nystrom et al. [10], Rodemann and Staude [6], Kim et al. [1], Szymczyk et al. [9], Lettmann et al. [2], and Benavente and Jonsson [17]) and surface streaming potential (e.g., Elimelech et al. [16], Childress and Elimelech [11], Blank et al. [7], Mockel et al. [8], Hagmeyer and Gimbel [12], Lettmann et al. [2], Peeters et al. [13], Childress and Elimelech [14], and Ernst et al. [15]).

Pore streaming potential is induced when the electrolyte solution flows through the membrane whereas surface streaming potential is induced when the electrolyte solution flows tangential to the membrane surface. Unlike some of the earlier streaming potential investigations (e.g., Tanny et al. [18], Kaneko and Yamamoto [19], Minning and Spiegler [20], and Khedr et al. [21]), the majority of the more recent investigations (e.g., Nystrom et al. [3], Elimelech et al. [16], Causserand et al. [4], Nystrom et al. [5], Nystrom et al. [10], Rodemann and Staude [6], Childress and Elimelech [11], Kim et al. [1], Blank et al. [7], Mockel et al. [8], Szymczyk et al. [9], Hagmeyer and Gimbel [12], Lettmann et al. [2], Childress and Elimelech [14], and Ernst et al. [15]) measure streaming potential over a range of solution pH. Investigating surface charge as a function of pH is crucial for understanding acid-base properties of membrane surface functional groups.

The majority of previous studies involved rather limited solution chemistries. In most cases, streaming potential measurements were performed using solutions containing simple electrolytes (e.g., Nystrom et al. [3], Elimelech et al. [16], Nystrom et al. [10], Kim et al. [1], Mockel et al. [8], Szymczyk et al. [9], Hagmeyer and Gimbel [12], Peeters et al. [13], Lettmann et al. [2], Benavente and Jonsson [17], and Ernst et al. [15]). Additional solution chemistries studied include solutions of bovine serum albumin (e.g., Causserand et al. [4] and Nystrom et al. [5]), human serum albumin (e.g., Rodemann and Staude [6] and Blank et al. [7]), and humics and surfactants (e.g., Childress and Elimelech [11] and Childress and Elimelech [14]). The bovine serum albumin, human serum albumin, humics, and surfactants were selected based on their prevalence in membrane feed waters. None of the above investigations, however, used actual membrane feed waters in the streaming potential measurements.

Ikeda et al. [22] used an electrophoresis method (rather than a streaming potential method) to evaluate zeta potential as a function of pH for an actual membrane feedwater. Specifically, a laser Doppler detector was used to evaluate the surface zeta potential of a thin-film composite RO membrane for several surfactant solution chemistries as well as for feedwater from a semiconductor plant. By matching zeta potential results for the membranes exposed to the actual membrane feedwater with results from the various surfactant solutions, it was determined that the cause of membrane fouling at the semiconductor plant was most likely due to the presence of a nonionic surfactant or a low concentration of a cationic surfactant. In this manner, streaming potential measurements were used as a preliminary diagnostic tool to identify a potential cause of membrane fouling.

The main objective of this paper is to investigate the effects of actual membrane feedwaters on the surface charge properties of two commercial RO membranes. The feedwaters selected for this investigation include tertiary wastewater effluent, which serves as membrane feedwater at the Orange County Water District (OCWD) (Fountain Valley, California) and river
water from the Brazos River (Brazos, Texas). To interpret the streaming potential results using these feedwaters, membrane streaming potentials were also evaluated in the presence of solution chemistries that directly relate to major chemical species found in typical membrane feedwaters. More specifically, the effects of divalent hardness cations (Ca\(^{2+}\)) and a humic acid are evaluated. Additionally, the effects of glutaraldehyde (a membrane storage agent) and atrazine (a pesticide) on membrane surface charge were evaluated. The mechanisms of surface charge acquisition by the RO membranes in the presence of the actual membrane feed waters, atrazine, and glutaraldehyde are delineated and discussed.

2. Experimental

2.1. Membranes

Two membranes, the TFC-HR and the TFC-ULP membrane, were obtained from Koch Membrane Systems (Wilmington, MA, USA) and evaluated in this investigation. The TFC-HR membrane is a proprietary thin-film composite RO membrane with additives in its active layer for enhancement of salt rejection. The manufacturer-reported water flux is 20–26 gfd and the salt rejection is 99.5% for 2000 ppm NaCl at 200 psi net driving pressure. The TFC-HR membrane was shipped as a dry rolled sheet with a polyvinyl alcohol (PVA) coating and a violet dye; the coating protects the membrane from abrasion during the rolling process and the violet dye identifies the presence of the coating. Both are rinsed off prior to membrane testing. After the PVA coating and violet dye were rinsed from the TFC-HR membrane, it was stored in deionized water at 5°C. The TFC-ULP membrane is an ultra-low pressure thin-film composite RO membrane. The manufacturer-reported flux rate is 25–30 gfd and the salt rejection is greater than 96% for NaCl and greater than 98% for MgSO\(_4\) for 2000 ppm NaCl and 5000 ppm MgSO\(_4\) at less than 100 psi net driving pressure. This membrane was received as a dry rolled sheet and was stored dry at room temperature.

2.2. Solution chemistries

The streaming potentials of both membranes were evaluated over the pH range of 3 to 9 for all solution chemistries. In order to determine a baseline, membranes were first evaluated with a background electrolyte solution of 0.01 M NaCl. Certified grade hydrochloric acid (HCl) and sodium hydroxide (NaOH) (Fisher Scientific, Pittsburgh, PA, USA) were used for pH adjustments and certified ACS grade sodium chloride (NaCl) salt (Fisher Scientific, PA, USA) was used as the background electrolyte.

The effect of a storage agent on streaming potential was investigated using 0.2% and 0.4% glutaraldehyde solutions. The recommended concentration for membrane storage is generally around 0.2%. The effect of a pesticide on streaming potential was investigated using Aatrex 4L (Ciba-Geigy, Ardsley, NY, USA). Aatrex 4L is a triazine herbicide which consists of 41% atrazine in ethylene glycol. In typical applications, the amount of pesticides in waters to be treated with membranes is in the ppb range. However, when testing membrane performance, pesticide dosages in the range of 20–30 ppm (close to solubility) are commonly used. For the streaming potential measurements, a concentration of 0.1 ppm was evaluated. After evaluating the streaming potential in the presence of the pesticide alone, Suwannee River humic acid was added to the solution and the streaming potential was reevaluated in the presence of both the pesticide and humic acid. The Suwannee River humic acid was received in a freeze-dried form from the International Humic Substances Society (Golden, CO, USA). The humic acid solution was made by dissolving the freeze-dried powder in deionized water and adjusting the pH to 7.5.
The effects of tertiary wastewater effluent were evaluated using lime-clarified secondary wastewater effluent that is used as membrane feedwater at OCWD. Following the lime clarification, the wastewater undergoes recarbonation to reduce elevated pH levels and multimedia filtration to reduce turbidity levels. The effects of a natural water were evaluated using Brazos River water. This feedwater was used because the membranes tested in this investigation were being considered for a water treatment plant fed by Brazos River water. A summary of water quality parameters for the OCWD membrane feedwater and the Brazos River water are shown in Table 1. The OCWD membrane feedwater has relatively high levels of TOC (16.4 mg/L) and Ca²⁺ ions (approximately 2 mM). The Brazos River water has a TOC concentration of 5.9 mg/L and Ca²⁺ concentration of approximately 0.45 mM. Additionally, the Brazos River water has a Mg²⁺ concentration of approximately 0.4 mM. In order to compare the effects of actual membrane feedwater with the individual effects of major chemical species found in these waters, the effects of 2 mg/L Suwannee River humic acid and 1 mM CaCl₂ were also evaluated. Certified ACS grade calcium chloride (CaCl₂) salt (Fisher Scientific, Pittsburgh, PA, USA) was used.

### Table 1

<table>
<thead>
<tr>
<th>Constituent conc., mg/L:</th>
<th>Brazos River water</th>
<th>OCWD water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.03</td>
<td>0.04</td>
</tr>
<tr>
<td>B</td>
<td>0.1</td>
<td>0.4</td>
</tr>
<tr>
<td>Ba</td>
<td>0.04</td>
<td>0.03</td>
</tr>
<tr>
<td>Ca</td>
<td>18.0</td>
<td>75.6</td>
</tr>
<tr>
<td>Fe</td>
<td>—</td>
<td>0.01</td>
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<tr>
<td>Mg</td>
<td>9.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Mn</td>
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<td>0.0008</td>
</tr>
<tr>
<td>Mo</td>
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<td>0.06</td>
</tr>
<tr>
<td>Na</td>
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<td>4.4</td>
</tr>
<tr>
<td>Ni</td>
<td>0.002</td>
<td>0.01</td>
</tr>
<tr>
<td>P</td>
<td>—</td>
<td>0.2</td>
</tr>
<tr>
<td>Zn</td>
<td>691</td>
<td>0.01</td>
</tr>
<tr>
<td>Conductivity, μS/cm</td>
<td>5.9</td>
<td>1383</td>
</tr>
<tr>
<td>TOC, mg/L</td>
<td>0.01</td>
<td>16.4</td>
</tr>
<tr>
<td>Turbidity, NTU</td>
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<td>0.09</td>
</tr>
<tr>
<td>pH</td>
<td>—</td>
<td>6.0</td>
</tr>
</tbody>
</table>

Note: — means below detectable limits.

The instrument, measurement procedure, and zeta potential calculation can be found elsewhere [11,16,26].

### 3. Results and discussion

#### 3.1. Indifferent electrolyte experiments

Zeta potential vs. pH data for experiments performed in the presence of 0.01 M NaCl are shown in Fig. 1. The TFC-HR and TFC-ULP membranes do not have isoelectric points in the pH range investigated (pH 3–9). The TFC-ULP membrane reaches a much more negative zeta potential (approximately −28 mV at pH 9) than the TFC-HR membrane (approximately −17 mV at pH 9). The shape of both zeta potential curves is indicative of amphoteric surfaces, or surfaces...
3.2. Glutaraldehyde experiments

The effect of 0.2% glutaraldehyde on the zeta potential of the TFC-HR membrane is shown in Fig. 2a. Glutaraldehyde appears to have a minimal effect on the zeta potential — making it slightly less negative. In the case of the TFC-ULP membrane (Fig. 2b), the 0.2% glutaraldehyde solution has almost no effect on the zeta potential and the 0.4% glutaraldehyde solution has a very small effect on the zeta potential — making it slightly less negative. Because the glutaraldehyde has no charged functional groups, it is not expected to influence the membrane surface charge. However, the minor effects for both membranes may be attributed to a slight shift in the electrokinetic plane of shear by the adsorbed glutaraldehyde molecules. In a previous investigation [11], the effects of storing membranes in a sodium meta-bisulfite (Na$_2$S$_2$O$_3$) solution were investigated. Unlike the glutaraldehyde, the sodium meta-bisulfite caused the membrane to be more negatively charged over
the entire pH range investigated. This effect was attributed to adsorption of the meta-bisulfite ($S_2O_3^{2-}$) ions.

3.3. Atrazine and humic acid experiments

The effects of atrazine, humic acid, and atrazine in combination with humic acid on the zeta potential of the TFC-HR membrane are shown in Fig. 3. Atrazine alone has little effect on the zeta potential of the TFC-HR membrane. Similar to the glutaraldehyde molecules, the atrazine molecules may cause a slight shift in the electrokinetic plane of shear which would result in a slightly less negative zeta potential. The humic acid alone causes the membrane to be more negatively charged over the entire pH range. The humic macromolecules readily adsorb to the membrane surface and the negatively-charged functional groups of the humics dominate the membrane surface charge [11,14]. The combination of atrazine and SRHA causes the membrane to be more positively charged than when the humic acid is tested alone. This suggests that atrazine adsorbs to the humic acid, thus reducing the adsorption of humic acid to the membrane surface.

3.4. OCWD membrane feedwater (tertiary wastewater effluent) experiments

Fig. 4 shows the effect of OCWD membrane feedwater on the zeta potential vs. pH behavior of the TFC-ULP membrane. For comparison purposes, the individual effects of 2 mg/L humic acid and 1 mM CaCl$_2$ on the zeta potential of the TFC-ULP membrane are also shown in Fig. 4. The OCWD membrane feedwater had a marked effect on the zeta potential of the membrane over the entire pH range. In the lower pH region, the OCWD membrane feedwater made the zeta potential more negative. The presence of organic acids in tertiary wastewater effluents may affect the zeta potential in the low pH range. As is
apparent from the graph of 2 mg/L humic acid, the effect of an organic acid is greatest at low pH where electrostatic repulsion between the membrane and the negatively-charged functional groups of the humic acid is lowest. This effect of humic acid on membrane zeta potential at low pH has been previously demonstrated for other RO membranes [11]. Characterization of the OCWD water (Table 1) reveals a relatively high TOC value (16.4 mg/L). The data from Table 1 also demonstrate that the OCWD water has a high calcium concentration (approximately 2 mM). Because the TFC-ULP membrane is negatively charged, complex formation of Ca²⁺ ions with the membrane surface would be electrostatically favorable [11]. Adsorption of Ca²⁺ to the membrane surface may reduce the negative charge of the membrane in the high pH region where less organic acid adsorption would be expected. Fig. 5 shows the effect of OCWD membrane feedwater on the zeta potential behavior of the TFC-HR membrane. The effect of the divalent cations in the OCWD membrane feedwater is greater for the TFC-HR membrane than the TFC-ULP membrane (Fig. 4); over the entire pH range investigated, the TFC-HR membrane is more positively charged. At low pH, the effect of the organic acids in the OCWD membrane feedwater is slight. The membrane is less positively charged in the presence of the OCWD membrane feedwater than it is in the presence of CaCl₂.

3.5. Brazos River Water experiments

Figs. 6 and 7 show the effect of Brazos River water on the zeta potential versus pH behavior of the TFC-ULP and TFC-HR membranes, respectively. The two most abundant ions in the Brazos River water are the divalent cations, Ca²⁺ (approximately 0.4 mM) and Mg²⁺ (approximately 0.45 mM). As explained above, the presence of divalent cations is likely to cause the zeta potential to be more positively charged due to complex formation of the divalent ions with
the membrane surface. The relatively high concentration of divalent cations (almost 1 mM) appears to outweigh the relatively low TOC concentration (5.9 mg/L); the result is a more positive zeta potential over the entire pH range for both membranes.

4. Conclusions

Results showed a more positive zeta potential in the presence of the Brazos River water, most likely due to the presence of divalent cations (Ca\(^{2+}\) and Mg\(^{2+}\)). For tertiary wastewater effluent, adsorption of organic acids in the wastewater effluent may have been the cause of the more negative zeta potential in the low pH range and the presence of divalent cations may have been the cause of the more positive zeta potential in the high pH range. Glutaraldehyde and atrazine showed little effect on the surface charge of the membranes. The minor effects may be attributed to a slight shift in the electrokinetic plane of shear by adsorbed glutaraldehyde or atrazine molecules. When atrazine was combined with humic acid, the atrazine reduced the effect of the humic acid and resulted in a less negative surface charge than when the humic acid was tested alone.

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References