Effect of humic substances and anionic surfactants on the surface charge and performance of reverse osmosis membranes

Amy E. Childress\textsuperscript{a*}, Shivaji S. Deshmukh\textsuperscript{b}

\textsuperscript{a}Department of Civil Engineering University of Nevada, Reno, Mail Stop 258, Reno, Nevada 89557-0152, USA

Tel. +1 (702) 784-6942; Fax +1 (702) 784-1390; email: amyec@unr.edu

\textsuperscript{b}Current address: Department of Civil and Environmental Engineering, University of California, Los Angeles, 3732 Boelter Hall, Los Angeles, CA 90095-1593, USA

Received 16 June 1998

Abstract

Streaming potential measurements were used to determine the surface zeta potential of two reverse osmosis (RO) membranes and to investigate the effect of solution chemical composition on membrane surface charge. Performance measurements were performed to evaluate the effect of membrane surface chemistry on membrane flux and rejection. The RO membranes evaluated were a thin-film composite polyamide membrane and an asymmetric cellulose acetate membrane. The solution chemistries investigated include Suwannee River humic acid and sodium dodecyl sulfate (an anionic surfactant). Zeta potential measurements revealed that in the presence of an indifferent electrolyte, both membranes had a positive zeta potential in the low pH range, passed through an isoelectric point between pH 2 and 3, and had a negative zeta potential in the mid to high pH range. Suwannee River humic acid and sodium dodecyl sulfate were found to readily adsorb to the membrane surface and markedly influence the membrane surface charge. Suwannee River humic acid had a significant influence on salt rejection at low pH where adsorption of the organic macromolecules caused a change in sign of the zeta potential (from positive to negative) and therefore a change in co-ion exclusion effects. The effects of the sodium dodecyl sulfate, also more apparent at low pH, were attributed to the formation of hemimicelles which caused decreased flux and increased salt rejection.

Keywords: Zeta potential; Streaming potential; Membrane charge; Membrane performance; Reverse osmosis membranes; Humic substances; Anionic surfactant

*Corresponding author.


0011-9164/98/$ – See front matter © 1998 Elsevier Science B.V. All rights reserved.
PII S0011-9164(98)00119-2
1. Introduction

As treatment regulations have become more stringent, greater research efforts have been put into the improvement of membrane processes. During the past decade, a variety of "new generation" water treatment membranes has been developed [1-4]. These membranes have been vastly improved in the areas of water flux, salt rejection, and especially in their ability to maintain high performance levels at substantially lower operating pressures than their predecessors.

Despite these improvements, a decline in membrane performance over time results from membrane fouling [5-9]. Fouling causes a decrease in the water flux across the membrane as well as an increase in salt passage through the membrane. It affects not only the performance of membranes, but also their longevity. Dissolved organics and colloidal matter, which are ubiquitous in natural waters, are considered to be the most serious foulants [5,9-11].

The interaction of organic and inorganic colloidal substances with membrane surfaces in aqueous media is dependent on the surface properties of the membrane [12-17]. Therefore, determination of membrane surface characteristics is critical to membrane fouling research. Surface characteristics have generally been overlooked in efforts to select optimal pretreatment schemes and operating conditions for various membrane separation processes.

The overall goal of this research was to characterize the surface zeta potential of two "new generation" water treatment membranes and to relate the performance of these membranes (i.e., water flux, salt rejection, and fouling behavior) to their surface characteristics. The objectives leading to this goal were: (1) to characterize the surface zeta potential of two polymeric RO membranes, (2) to evaluate the flux and rejection of these membranes for solution chemistries typical of those found in natural waters, and (3) to relate the performance to the surface characteristics.

2. Experimental

2.1. Reverse osmosis membranes

Two membranes were investigated: a thin-film composite polyamide RO membrane (FT-30, FilmTec, Minneapolis, MN) and an asymmetric cellulose acetate RO membrane (CG, Desalination Systems, Escondido, CA). The thin-film composite membrane was stored in deionized water at 5°C and the cellulose acetate membrane was stored dry.

2.2. Streaming potential analyzer

Streaming potential measurements were performed with the BI-EKA, a commercial apparatus from Brookhaven Instruments Corp., Holtsville, NY. This instrument utilizes silver/silver chloride electrodes to measure the streaming potential that is induced when an electrolyte solution flows across a stationary, charged membrane. Zeta potential is calculated from the measured streaming potential using the Helmholtz-Smoluchowski equation [18,19] with the Fairbrother and Mastin substitution [20]. A detailed description of this instrument, the measurement procedure, and the zeta potential calculation can be found elsewhere [21,22].

2.3. Solution chemistries

Each membrane was evaluated over the pH range of 3 to 9 for each solution chemistry. The solution chemistries selected for this investigation represent chemical species found in natural waters and wastewaters. Included are the effects of Suwannee River humic acid and sodium dodecyl sulfate (an anionic surfactant). The Suwannee River humic acid was received in a freeze-dried form from the International Humic Substances Society (Golden, CO). The humic acid solution was made by dissolving the freeze-dried powder in deionized water and adjusting the pH to 8.2. The sodium dodecyl sulfate was certified grade (Fisher
Scientific, Pittsburgh, PA). All experiments were performed with a background electrolyte concentration of 0.01 M NaCl.

2.4. Reverse osmosis test unit

The performance of the membranes under the various solution chemistries was evaluated using a closed-loop membrane test unit. In this unit, the test solution is pumped from a solution reservoir, through two membrane cells (in parallel), and back to the reservoir. The membrane cells operate in cross-flow mode and both the permeate and concentrate are recycled. The temperature of the system is kept constant at 20°C, and the pressure and flow rate are monitored during the entire run.

2.5. Reverse osmosis performance tests

The membranes for each run were taken from storage, placed in the membrane cells, and given 45 minutes of hydration. The sample chamber or surface chamber was filled immediately after the stabilization period. Prior to making any measurements, there were two 30-min equilibration periods during which the flux was monitored. If the flux was constant over these equilibration periods, the measurements were started. Performance was first evaluated at ambient pH (pH~5.7). The solution was then adjusted to pH 9 by the addition of NaOH. From pH 9, the pH was incrementally dropped to pH 3 by additions of HCl and performance was evaluated at each pH unit. After pH 3, the pH was raised back to pH 5.7 and the performance was evaluated there to ensure that permanent fouling had not occurred and that the initial flux and rejection were maintained.

3. Results and discussion

3.1 Zeta potential measurements

Zeta potential results (Fig. 1) reveal that in the absence of humic substances (hollow symbols), both membranes are positively charged at low pH, have an isoelectric point between pH 2 and 3 and are negatively charged at high pH. More specifically, the isoelectric points of the FT-30 and CG membranes are 3.0 and 2.4, respectively. Zeta potential curves of this shape are characteristic of amphoteric surfaces, or surfaces with both acidic and basic functional groups. In the presence of Suwannee River humic acid (Fig. 1, solid symbols), the membranes become more negatively charged over the entire pH range. This indicates that the humic macromolecules readily adsorb to the membrane surface and that the negatively-charged functional groups of the humics dominate the membrane surface charge.

The presence of Suwannee River humic acid has virtually the same effect on both membranes at low pH where their isoelectric points no longer exist (Fig. 1). At low pH, where the membrane and humic acid are oppositely charged, adsorption of
the humic acid is favorable because of both electrostatic and hydrophobic interactions. At higher pH values where the humic acid and membrane are similarly charged, adsorption is likely to be dominated by hydrophobic interactions. The effect of the Suwannee River humic acid in the higher pH range varies. In the case of the CG membrane, only minimal adsorption occurs because of the electrostatic repulsion between the humic acid and the membrane surface and the increased hydrophilicity of the humic acid [22]. For the FT-30 membrane, the humic appears to continue adsorbing at pH 8 and 9 and, therefore, the membrane becomes more negatively charged.

As seen in Fig. 2, the effect of the anionic surfactant (sodium dodecyl sulfate) is somewhat similar to the effect of the humic substances in that the negatively-charged sulfate functional groups of the surfactant molecules cause the membrane to become more negatively charged. The adsorption characteristics of surfactants are governed by the molecular structure of the surfactant molecules (e.g., type of polar head, structure and length of hydrocarbon chain) and the characteristics of the membrane surface (e.g., charge, hydrophobicity) [23–25].

The effect of the surfactant on the membrane zeta potential can be accounted for using the concept of hemimicelle formation, as initially proposed by Gaudin and Fuertenau [26]. Hemimicelles result from the surfactant ions associating with each other to remove their hydrocarbon chains from the bulk water and, hence, to reduce the free energy of the system [27]. Hemimicelles, or two-dimensional surfactant aggregates, form at the solid-solution interface when the hemimicelle concentration (HMC) of the system has been exceeded. The HMC is the point at which there is a sharp increase in adsorption which reflects the transition from individual surfactant ion adsorption to surfactant association at the surface through lateral interaction of the hydrocarbon chains [27]. In Fig. 2, with $10^{-3}$ M sodium dodecyl sulfate, it is expected that the HMC for the system has been exceeded [22] and that hemimicelle formation is responsible for the significantly negative zeta potential.

### 3.2. Performance measurements

In the case of the FT-30 membrane (Fig. 3), the presence of Suwannee River humic acid causes a slight decrease in flux and a slight increase in salt rejection over the entire pH range. The increase in salt rejection becomes more substantial at low pH where the membrane is now negatively charged due to the negatively-charged functional groups of the humics that are adsorbed to the membrane surface [28]. When humic acid was not present, salt rejection was lower at pH 3 since the membrane was positively charged; however, in the presence of humics, salt rejection is higher at pH 3 due to an increase in co-ion exclusion effects. In other words, because the membrane is negatively
charged, the chloride ions are better rejected at low pH. By electroneutrality, sodium rejection also improves. Investigations of individual ion (i.e., sodium and chloride) rejection confirm this; results from these investigations can be found elsewhere [29]. For the CG membrane (Fig. 4), the presence of Suwannee River humic acid causes no changes in flux and salt rejection with one exception. At pH 3, salt rejection increases slightly due to co-ion exclusion effects.

Unlike Suwannee River humic acid, sodium dodecyl sulfate has significant effects on the flux and salt rejection of both membranes (Figs. 5 and 6). The anionic surfactant temporarily alters the charge and hydrophobicity of the membrane. Convective adsorption of the sodium dodecyl sulfate results in a secondary filtration layer on the membrane surface which increases the resistance to flow through the membrane. The overall result is a decline in flux and increase in salt rejection.

The flux of both membranes (especially the FT-30) was significantly reduced upon introduction of the sodium dodecyl sulfate to the system. Therefore, the operating pressure of the FT-30 membrane was increased in order to obtain adequate flux through these membranes. Nonetheless, for the FT-30 membrane, flux was lower over the entire pH range (Fig. 5a). For the
CG membrane (Fig. 6a), flux was slightly lower over the entire pH range.

As can be seen in Figs. 5b and 6b, salt rejection increases at low pH (more significantly for the FT-30 membrane) and is relatively unaffected at high pH. The effect of the anionic surfactant on flux and salt rejection is most apparent at low pH because at low pH the membrane is positively charged and therefore, electrostatically attracts the negatively-charged head groups of the surfactant ions. When the negatively-charged head groups of the surfactant molecules are aligned towards the membrane surface, the hydrocarbon chains of the surfactant will dangle in the bulk solution. Because this is not a thermodynamically favorable formation for the hydrocarbon chains, the hydrocarbon chains of the surfactant ions on the surface will associate with the hydrocarbon chains of the surfactant ions in the bulk solution in order to reduce the free energy of the system [27]. The resulting hemimicelles will decrease the flux and increase the salt rejection of the membrane. This situation would not be as likely to occur at high pH since the membrane is no longer positively charged. Instead, at high pH, the hydrocarbon chains will be attracted to the membrane surface, leaving the negatively-charged head groups to dangle in solution. Although some surfactant
association may take place, it would be substantially less than at low pH since the hydrocarbon chains of the surfactant ions are in a thermodynamically favorable formation.

4. Conclusions

Zeta potential results were found to be significantly influenced by humic acid and surfactant adsorption. In the presence of an indifferent electrolyte (NaCl), the membranes are positively charged in the low pH range, pass through an isoelectric point between pH 2 and 3, and are negatively charged in the high pH range. In the presence of Suwannee River humic acid or sodium dodecyl sulfate, the membranes are negatively charged over the entire pH range.

Overall, the Suwannee River humic acid had little effect on the performance characteristics of both membranes. There was only a slight decrease in overall flux on the FT-30 membrane implying that this membrane was more susceptible to fouling by the humic acid. Otherwise, the Suwannee River humic acid had the most influence on salt rejection at low pH where adsorption of the organic macromolecules caused a change in sign of the zeta potential (from positive to negative) and therefore a change in cation exclusion effects.

The more dramatic effects of the anionic surfactant on the performance characteristics of the membranes are accounted for using the concept of hemimicelle formation. The sodium dodecyl sulfate hemimicelles that form on the membrane surface act as a secondary filtration layer. Particularly at low pH, this layer causes decreased flux and increased salt rejection.

References


