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# Indirect determination of zeta potential at high ionic strength: Specific application to semipermeable polymeric membranes

Bryan D. Coday [a], Thomas Luxbacher [b], Amy E. Childress [c], Nohemi Almaraz [a], Pei Xu [d], Tzahi Y. Cath [a,*]

[a] Colorado School of Mines, Golden, CO, USA
[b] Anton-Paar GmbH, Graz, Austria
[c] University of Southern California, Los Angeles, CA, USA
[d] New Mexico State University, Las Cruces, NM, USA

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## ABSTRACT

The understanding of membrane charge neutralization and diffuse layer compression at environmentally relevant ionic strengths is becoming increasingly important. In this work, the impact of high ionic strengths on membrane zeta potential was determined using a combination of streaming potential measurements and theoretical modeling. Streaming potential measurements were conducted on cellulose triacetate (CTA) and polyamide thin-film composite (TFC) membranes at ionic strengths within the operating limits of an electrokinetic analyzer. Zeta potential calculated from streaming potential was then extrapolated to environmentally relevant ionic strengths (0.05 to 1 M 1:1 electrolyte) using the Debye–Hückel and Helmholtz-Smoluchowski models. Extrapolated zeta potential values revealed that membrane charge neutralization and compression of the diffuse layer are limited by the size of the hydrated counter-ions, and full membrane charge neutralization, or even charge reversal, can not be achieved. The expected zeta potential of CTA membranes was similar to that of TFC membranes at high ionic strength, which has considerable implications in the comparison of membrane performance when treating brackish and saline feed waters. The methodologies developed in this work can help to better understand the contribution of electrostatic forces resulting from zeta potential to the sum of interfacial forces present at the membrane surface.

## 1. Introduction

Membranes are rapidly becoming the leading separation method in a broad range of applications, including treatment of highly impaired waters. This is especially true for semipermeable polymeric nanofiltration (NF), reverse osmosis (RO), and forward osmosis (FO) membranes. NF and RO are pressure-driven membrane processes most commonly employed in brackish water and seawater desalination. They have also been used for treatment of reclaimed water from domestic wastewater in a variety of water reuse scenarios [1,2] and for applications in the food and beverage industry [3–5]. FO is an osmotically driven membrane process where the driving force for mass transfer is the difference in chemical potential between a concentrated draw solution and a lower salinity feed solution [6–14]. Therefore, FO membranes may be exposed to high ionic strengths on both sides of the membrane, resulting in unique mass transport and contaminant rejection phenomena [15–20]. FO is considered an advanced pretreatment method for downstream pressure-driven membrane processes and has been investigated for treatment of complex feed streams, including anaerobic digester centrate and activated sludge [21–26], landfill leachate [27], hypersaline streams in the mineral recovery industry [28], and exploration and production wastewaters in the oil and gas industry [6,12,29,30].

The fouling propensity of RO, NF, and FO membranes and mass transport through them are largely dependent on the feed stream characteristics and the complex interactions occurring near the membrane surface. Operating conditions impact the transport mechanisms by which feed stream contaminants (solutes, colloids, and particles) approach the membrane surface and the physico-chemical characteristics of the membrane polymer and contaminants govern the interfacial attraction and adhesion forces at the membrane surface. Interfacial attraction and adhesion forces are commonly expressed as the sum of electrostatic, acid–base, van der Waals, and hydrophobic forces between the membrane polymer and feed stream contaminants [31]. Surface charge and hydrophobicity are of particular significance in the development

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* Correspondence to: Colorado School of Mines, 1500 Illinois St., Golden, CO, 80401; USA. Tel.: +1 303 273 3402; fax: +1 303 273 3413.
*E-mail address:* tcath@mines.edu (T.Y. Cath).

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of interfacial force models such as the extended Derjaguin–Landau–Verwey–Overbeek (XDLVO) model, which has been used to explain and predict membrane–foulant interactions [31–36]. Electrostatic and hydrophobic interactions are also dominant mechanisms affecting the rejection and transport phenomena of charged and uncharged solutes, respectively, in semipermeable membrane processes [37–45].

Semipermeable membranes acquire surface charge when in contact with aqueous solutions. This surface charge impacts the spatial distribution and concentration of dissolved solutes at the membrane–solution interface, resulting in the formation of an electric double layer (EDL) [46–48]. Surface charge cannot be measured directly; instead, the zeta potential ($\zeta$), or the electrical potential at the plane of shear between the stationary and mobile parts of the EDL (the slipping or shear plane) can be determined. The zeta potential of flat membrane surfaces is calculated from streaming potential, which is most commonly measured using an electrokinetic analyzer [49]. The acidity and degree of ionization of the membrane surface, and the pH and ionic strength of the electrolyte solution influence streaming potential.

Electrokinetic analyzers can measure streaming potential at all pH values relevant to membrane treatment applications; however, determination of streaming potential, and thus the calculation of zeta potential, has been limited to relatively low ionic strength solutions ($<0.1$ M) [50–52]. The ionic strength at which streaming potential can be reliably measured by commercial electrokinetic analyzers is limited by the sensitivity of their potential measurement devices (200–500 $\mu$V). When the ionic strength exceeds a certain value, the streaming potential signal assumes values below the acceptable threshold for electrode polarization. The ability to experimentally evaluate the impacts of ionic strength on membrane diffuse layer compression and electrostatic charge shielding using existing electrokinetic analyzers is thus limited to salinities below those of most desalination feed streams and brines.

The Gouy–Chapman–Stern theory and recent modifications have described electrostatic shielding of charged surfaces at increasing ionic strength [53]. These theories predict that counter-ions, most commonly modeled as point charges, aggregate in the Stern layer adjacent to the membrane surface. The concentration of counter-ions in the Stern layer increases with ionic strength until the charged surface is neutralized and the diffuse layer collapses [54]. The ability to estimate membrane zeta potential at increasing ionic strength with these models is limited because ions are hydrated and will exhibit a considerable spatial extension. Therefore, it is likely that the concentration of counter-ions within the Stern layer is limited and complete charge neutralization will not occur. Consequently, XDLVO theory (and similar) assessments of membrane–contaminant interactions using current zeta potential assessment techniques or predictions from the Gouy–Chapman–Stern theory (and similar) may not accurately predict the contribution of electrostatic forces to the sum of interfacial interactions near the membrane surface in current and emerging treatment applications.

The main objective of this study was to develop a comprehensive understanding of electrostatic charge shielding and compression of the diffuse layer as described by the EDL model (and similar). Specifically, the impact of high ionic strength on membrane zeta potential was investigated using a combination of streaming potential measurements and theoretical modeling. A series of streaming potential experiments were conducted on three polymeric membranes at increasing ionic strength (1:1 electrolyte) using an electrokinetic analyzer. Using the Debye–Hückel and Helmholtz–Smoluchowski models, zeta potential results from measurements with electrolyte ionic strength less than 0.05 M were extrapolated to environmentally relevant ionic strengths (0.05–1 M). The methodologies presented in this study provide a more holistic understanding of the interfacial forces near the membrane surface in brackish and saline environments. FO membranes were used in this study due to surging interests in the treatment of hypersaline and complex feed streams using FO; however, the methodology presented is also applicable to other material–water interfaces beyond semipermeable polymeric membranes.

## 2. Materials and methods

### 2.1. Membranes

Three flat sheet FO membranes were investigated. An asymmetric cellulose triacetate (CTA) membrane and a thin-film composite (TFC) polyamide membrane (designated TFC1) were obtained from Hydration Technology Innovations (HTI) (Albany, OR). A second TFC polyamide membrane (designated TFC2) was obtained from Oasys Water (Boston, MA).

All membranes were supplied hydrated and were stored in a refrigerator at approximately 5 °C. Prior to all experiments, membrane coupons were thoroughly rinsed and then stored in deionized water at 5 °C for 24 h. Rinsed coupons were dried in a desiccator at room temperature for 24 h prior to characterization.

### 2.2. Solution chemistry

Deionized water (EMD MilliPore, Billerica, MA) and certified ACS-grade potassium chloride (KCl) (Fisher Scientific, Fair Lawn, NJ) were used for preparing the electrolyte solution. For streaming potential measurements, five concentrations (0.001, 0.002, 0.01, 0.03, 0.05 M) of KCl were used, all of which were well below the electrode polarization threshold (0.1 M) of the electrokinetic analyzer used in this study. In one additional set of experiments, lithium chloride (LiCl) and sodium chloride (NaCl) (Fisher Scientific, Fair Lawn, NJ) electrolyte solutions were used at the same molarities as KCl. The goal of employing two additional monovalent solutes was to corroborate the effects of counter-ion hydration radius on membrane charge shielding at high ionic strength.

### 2.3. Measurement of membrane zeta potential

Streaming potential, which can be measured directly or calculated from streaming current and cell resistance measurements using Ohm's law, was measured using a commercial electrokinetic analyzer (SurPASS, Anton-Paar GmbH, Austria). Dried membrane coupons were mounted on a SurPASS adjustable-gap cell that accommodates small planar samples with a rectangular size of $20\times 10\ \mathrm{mm}^2$. The cell was mounted on the electrokinetic analyzer and the hydraulic system and gap between the membranes were flushed with deionized water for approximately 2 min. The system was then drained and flushed twice with electrolyte solution to ensure that all deionized water was removed. The electrolyte solution was replaced and recirculated for at least 30 min. This neutralized any localized charge on the Ag/AgCl electrodes and minimized variability in streaming potential measurements [39].

All streaming potential measurements were performed at approximately 22 °C with an average gap height of $116\pm 2$ μm. At least eight streaming potential measurements (four flowing from left to right and four from right to left) were recorded at each ionic strength and then averaged to calculate the zeta potential. The pH of the electrolyte solution was not varied during this study. For each membrane type, the same coupon was used for all ionic strengths to minimize experimental error due to changes in membrane physiochemical properties and setup of the adjustable-gap cell. The range of standard deviation observed for all membrane zeta potential measurements was 0.1–1.1 mV. This range of standard deviation is well below that