

Characterizing Membrane Surface Charge by Contact Angle Titration

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ABSTRACT

Accurate characterization of membrane surface charge is vital for understanding membrane surface chemistry, separation performance, and fouling resistance. Streaming potential is the standard electrokinetic phenomena used to characterize a membrane's isoelectric point and zeta potential, which is related to the dynamic charge functionality at the membrane-solution interface as function of solution pH and ionic composition. We have recently developed a new method for directly measuring membrane surface charge via direct surface titration. Direct surface titration enables identification of maximum surface charge density, fractional ionization as a function of pH, and the apparent pKa of a charged surface. We have employed this new characterization technique to assess the charge of several commercial polyamide reverse osmosis membranes and compare these results to charge determined from classical electrokinetic measurements.

INTRODUCTION

Reverse osmosis (RO) and nanofiltration (NF) membrane processes are on the cutting edge of water treatment today, and thus, their development and application require more direct and reliable characterization techniques. Specifically, accurate characterization of membrane surface charge is vital for understanding RO/NF membrane separation performance as well as surface fouling phenomena. Surface fouling is caused by the adsorption, deposition, or crystallization of rejected matter on the membrane surface and/or within membrane pores. The principal consequence of membrane fouling is an increased hydraulic resistance, and thus, greater energy required to operate the filtration process. Fouling is one of the biggest hurdles associated with membrane desalination, and thus, it is crucial to be able to understand and reduce the fouling propensity of RO/NF membranes. Electrokinetic phenomena, particularly streaming potential, are often used to characterize a membrane surface (zeta) potential, which is related to the charge functionality at the membrane-solution interface as well as the solution pH and electrolyte composition. While zeta potential is an important parameter for understanding colloidal and interfacial phenomena, it is an indirect, relative description of membrane surface charge. In particular, streaming potential depends on electrolyte composition and may be highly misleading due to specific ion adsorption and surface conductance related phenomena. Our objective is to develop a rapid technique to characterize directly the charge functionality of polymeric membranes.

EXPERIMENTAL METHODS

Contact angle titration involves measuring sessile drop equilibrium contact angles on a membrane surface using both buffered and unbuffered aqueous solutions adjusted to a range of pH values. The sessile drop contact angle technique measures the angle between the baseline of a liquid drop and the tangent at the liquid/surface boundary. This angle is a basic measurement of surface wettability (i.e. hydrophobic/hydrophilic) and is governed by Young's Equation:

$$0 = \gamma_{SV} - \gamma_{SL} - \gamma_{LV} \cos \theta \quad (1)$$

where γ_{SV} is the solid-vapor interfacial free energy, γ_{SL} is the solid-liquid interfacial free energy, γ_{LV} is the liquid-vapor interfacial free energy, and θ is the experimental contact angle. Young's equation is essentially a thermodynamic equilibrium equation where the chemical potential of all three phases are equal. Young's equation gives more in depth insight into the principles governing contact angle titration and shows how the ionic charge of the solid surface influences the contact angle. If it is assumed that the only change during titration occurs at the solid-liquid interface then as the surface becomes more ionized its solid-liquid surface free energy increases resulting in a drop in contact angle and thus a more hydrophilic or wettable surface.

This behavior is best observed during the buffered titration experiments in which a series of contact angle measurements are performed using aqueous buffered solutions at a range of pH values (2-12). Using buffered drop solutions eliminates the influence of surface functional groups on the pH of the drop, which effectively act to buffer the drop of unbuffered solutions. By maintaining a constant drop pH the hydroxide ion concentration in the solution can directly react with the solid surface by means of ionization of the surface functional groups. Hence, the inflection point of the buffered contact angle titration curve provides the apparent dissociation constant (pKa) for the predominant type of surface ionizable groups, while the local contact angles of the buffered solution provide the extent of surface ionization with respect to pH.

The ionization curve gives the relationship between the fraction of ionized functional groups and the pH of the drop solution. There are three distinct regions to the ionization curve: the upper region, the transition region, and the lower region. In the case of acidic surfaces (i.e. when the membrane surface is characterized by the concentration of surface carboxylic acids), the upper region is present at low pH values and describes the region of surface neutrality (where there is no ionization and the surface contains only carboxylic acid groups RCOOH). The lower region is present at high pH values and represents the region of complete ionization (where all surface carboxylic acids are deprotonated and exist as carboxylate ions COO⁻). The transition region is what represents the region of fractional ionization and gives the apparent dissociation constant.

A series of unbuffered titration experiments are also performed to give insight into the chemical composition of the solid surface. As opposed to the buffered titration, the unbuffered drop liquid does not maintain a constant pH as it is effectively buffered by the surface functional groups. Therefore the breakpoint of unbuffered titration curves gives the point in which the buffering due to the ionizable functional groups at the surface fails and thus gives the net concentration of surface ionizable groups (proportional to acid or base concentration in solution). From the net concentration of surface ionizable groups we can then determine the surface charge density using known parameters of molecular charge and distribution.

RESULTS AND DISCUSSION

Effectively, we are determining the fractional ionization and apparent dissociation constant from the buffered titration experiments and the surface charge density from the unbuffered titration experiments. Contact angle titration differs from traditional titrimetric methods because it deals only with the surface functionality and does not require further analysis of the titrant solution.

Figure 1 shows the data results for the buffered contact angle titration of two commercially available reverse osmosis membranes XLE and SG. SG is a relatively smooth,

hydrophilic, and acidic reverse osmosis membrane manufactured by GE Osmonics characterized with a salt rejection of 97%. XLE is a slightly rougher and more hydrophilic acidic reverse osmosis membrane manufactured by Dow-Film Tec and has a similar salt rejection of 96%. From previous streaming current measurements it is also known that SG is typically more negatively charged than XLE. From Figure 1 the transition region between pH ~6 and pH~9 gives the fractional ionization, α , as a function of pH.

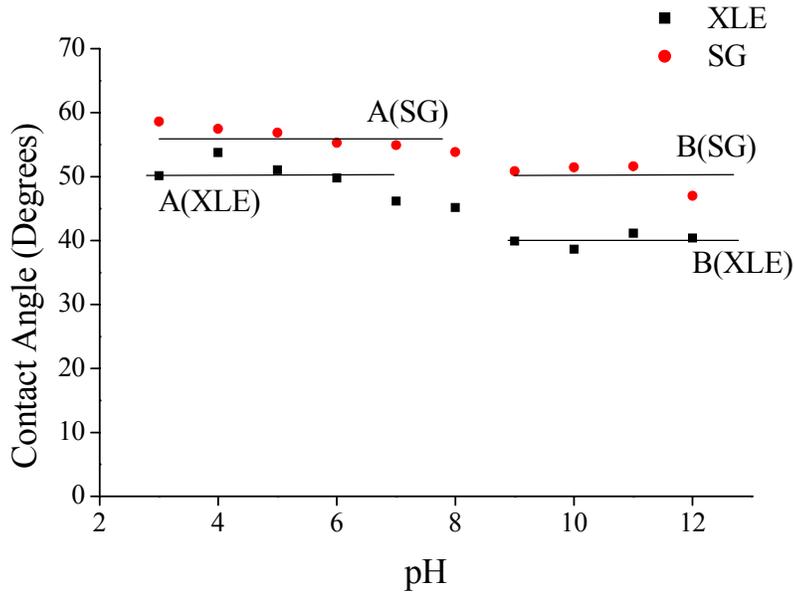


Figure 1 Buffered Titration of RO Membranes XLE and SG

Figure 2 shows the data results for the unbuffered contact angle titrations on the same two commercial RO membranes. The pH in which the titration curve breaks thus indirectly gives the maximum surface charge density, σ_0 , from the known concentration of hydroxide ions in solution.

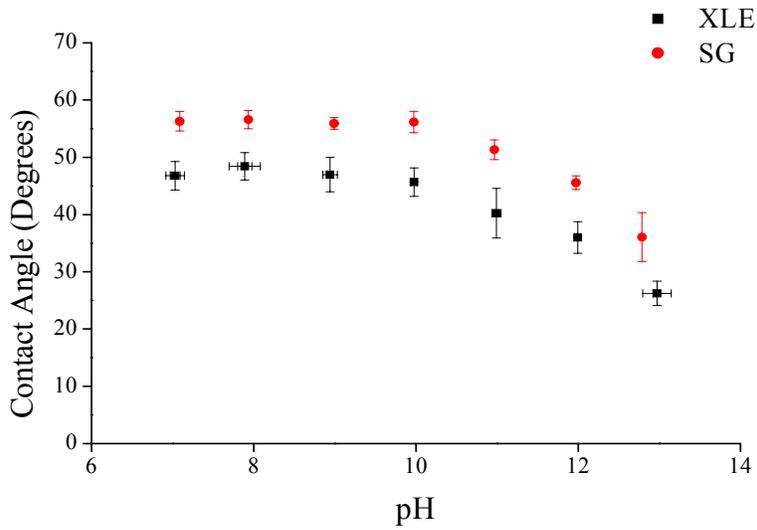


Figure 2 Unbuffered Titration for RO Membranes SG and XLE

These determined properties were then used to calculate the zeta potential using a combined form of the Grahame equation and the Gouy-Chapman model (Equations 2 and 3)

$$\sigma = \alpha\sigma_0 = 0.117 \sinh\left(\frac{\zeta}{51.4}\right) \sqrt{[\text{NaCl}] + 10^{-\text{pH}}}$$

$$\sigma = e[\text{COO}^-]_0 = e[\text{OH}^-]; \quad \alpha = \frac{\cos \theta - \cos A}{\cos B - \cos A}$$

Equations 2 & 3 Zeta Potential

The final results are a calculated zeta potential, ζ , vs. pH plot (Figure 3), which was then compared to a similar plot determined by a streaming potential analyzer (Figure 4).

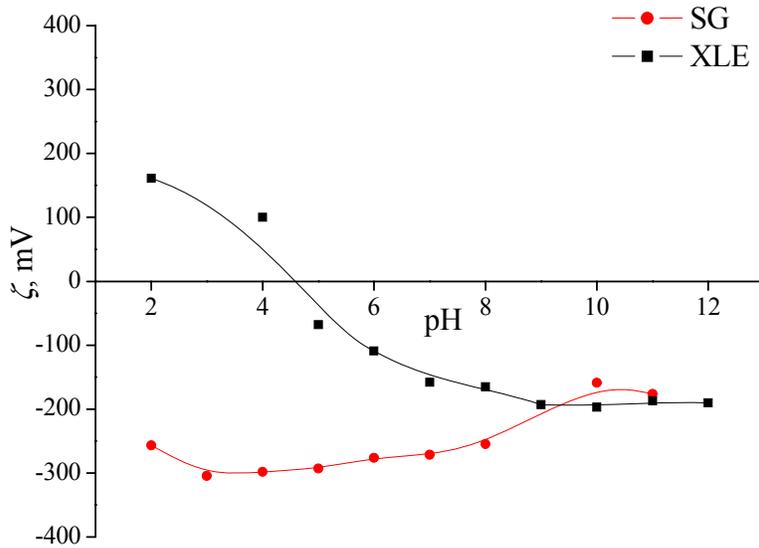


Figure 3 Contact Angle Titration Determined Zeta Potential

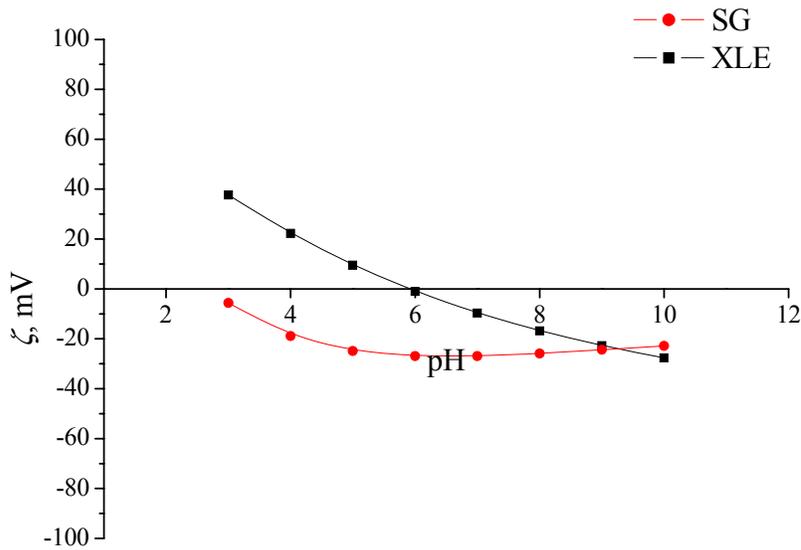


Figure 4 Streaming Current Analyzer Determined Zeta Potential

These results show that the contact angle measurement technique is accurate in that it can predict qualitative trends with respect to membrane surface charge and zeta potential. However, it can also be noted that there is about an order of magnitude difference between numerical values of the zeta potentials, which is due to the oversimplification of the contact angle titration technique (i.e. not taking into account surface roughness, oversimplification of membrane surface chemistry characteristics). This difference should not be taken at face value because it is

yet unclear how accurate the streaming current analyzer is and therefore it shouldn't be used as a numerical reference for "true" zeta potential.

CONCLUSIONS

Contact angle titration is a relatively accurate and direct measurement of surface charge parameters such as surface charge density and zeta potential. The method utilizes the measurement of equilibrium contact angles for both buffered and unbuffered drops at a range of pH values. The subsequent buffered titration curve predicts the fractional surface ionization plot and the unbuffered titration curve determines the maximum surface charge density. When experimenting the technique on two commercial acidic RO membranes, the contact angle titration method correctly determined the expected zeta potential trend with respect to pH. Considering how the general purpose of the technique is for comparative analysis, the fact that it might not be completely accurate numerically is not as big of a concern. However, there is still room for improvement with respect to refining the technique to account for surface roughness and more complicated surface chemistries.

REFERENCES

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