

Does the surface zeta potential approach zero at high salinity?

*Thomas Luxbacher¹⁾, Bryan Coday²⁾ and Tzahi Cath²⁾

¹⁾ Anton Paar GmbH, 8045 Graz, Austria

²⁾ Department of Civil and Environmental Engineering, Colorado School of Mines,
Golden, CO 80401, USA

¹⁾ thomas.luxbacher@anton-paar.com

ABSTRACT

The electrokinetic potential, aka the zeta potential, has gained importance for the surface analysis of membranes and filters of various kinds. A significant number of membrane zeta potential results presented in the literature refer to the analysis of flat sheet polymer membranes for nanofiltration and reverse osmosis. These membranes play a major role in the process of seawater desalination. When in use, the membrane surfaces get exposed to feed water with high salinity while the zeta potential is commonly determined in the presence of a dilute aqueous solution of a simple electrolyte. Although the discrepancy in the ionic strength between measurement and filtration does not reduce the quality of information gained from the zeta potential analysis, it is desirable to know the effective charge at the membrane-feed water interface under environmental conditions. We present an analytical approach to obtain reliable zeta potential data at high ionic strength corresponding to seawater and brines of even higher salinity despite of the experimental restriction to measurements at 0.1 mol/l and below.

1. INTRODUCTION

The solid surface zeta potential informs about the charging behavior at the interface between a solid material surface, such as a polymer membrane, and a surrounding aqueous solution. Furthermore the zeta potential introduces the driving force for electrostatic attraction and repulsion between the membrane surface and approaching solutes in the aqueous solution. The knowledge of the zeta potential is therefore required to predict the rejection of ions and other charged compounds by ultrafiltration and nanofiltration membranes. It further determines the partitioning of ions in processes such as reverse and forward osmosis.

Besides this direct correlation between the zeta potential with salt rejection and related processes in membrane separation, it is an important indicator for surface functional groups. These chemical entities of the membrane surface, e.g., carboxylic acid or amine groups, render the surface acidic, amphoteric or basic and are responsible for the charge formation. The interaction of these groups with water is

driven by acid and base reactions and therefore strongly dependent on the pH value of the aqueous solution, which is applied to probe the membrane surface. Another mechanism for the formation of interfacial charge, which is especially predominant for hydrophobic surfaces such as pristine polymer films, is the accumulation of water ions (hydroxide, OH^- , and hydronium, H_3O^+) on the solid surface (Zimmermann 2010). This latter mechanism is likely to dominate the interfacial charge formation on polymer membranes, which exhibit only a small surface concentration of functional groups. The contribution of water ions makes the charging of a polymer surface again pH dependent. However, the evolution of zeta potential with pH differs significantly for functionalized solids and hydrophobic surfaces which lack any functional groups (Bellmann 2002).

Finally the zeta potential may be applied to investigate the interaction of solutes present in the aqueous solution with membrane surfaces. Complex solutes such as divalent or even trivalent cations and anions or organic residues in feed water may get specifically adsorbed on the membrane surface thus altering the zeta potential. While the adsorption of organics and macromolecules such as surfactants, humic acid or even nanoparticles may be visualized by a time-resolved recording of changes in the surface zeta potential (Ripoll 2012), the effect of ions are best assessed by the recording of the zeta potential with increasing salt concentration.

The solid surface zeta potential of macroscopic solids is determined from the measurement of streaming potential and streaming current (Luxbacher 2006). Commercial instrumentation for the streaming potential measurement and thus for the determination of the solid surface zeta potential limit the analysis to an ionic strength of 0.1 mol/l. This upper limit is below the salinity of seawater and other brines with even higher ionic strength. Since feed water with such high salinity gets exposed to membrane surfaces during the filtration process, it would be desirable to obtain knowledge about the interfacial charge and zeta potential, if there is any, under such conditions. The possibility of the zeta potential analysis across five orders of magnitude of ionic strength makes it likely to extrapolate the measured data to an ionic strength slightly or even significantly higher than 0.1 mol/l. We present an analytical approach for such an extrapolation which is based on the dependence of streaming potential on ionic strength. With this approach, it is not only possible to obtain information about the membrane-water interfacial charge at high salinity and complex feed water composition. The results furthermore suggest that the zeta potential levels off at high salinity. This is in contradiction to the prediction of the model of the electrochemical double layer which forecasts that the zeta potential will vanish at high ionic strength. We explain the contradictory observation by the steric hindrance of counter ions in the stagnant water layer of the solid/liquid interface.

2. EXPERIMENTAL

The zeta potential of thin-film composite polyamide membranes for forward osmosis TFC1 (Hydration Technology Innovations, Albany, OR, USA) and TFC2 (Oasys Water, Boston, MA, USA) was determined in the presence of an aqueous solution of KCl at different ionic strength. A pair of FO membranes with 20 mm x 10 mm size was soaked in deionized water for 12 hours prior to the mounting on sample holders of the adjustable gap cell of the SurPASS electrokinetic analyzer (Anton Paar, Austria). The

measurement of streaming potential, streaming current, and the electrical resistance were performed in KCl with 0.002, 0.015, and 0.04 mol/l. For the extrapolation of zeta potential to high salinity condition, the streaming potential coefficient $dU_{str}/d\Delta p$, i.e., the slope of the linear dependence of streaming potential on the differential pressure, was used. In order to support the proposed approach, the zeta potential of a glass slide was determined at various ionic strengths in the range of 10^{-6} - 10^{-1} mol/l. Furthermore measurements of streaming potential were performed on such glass slide in the presence of 0.15 mol/l and 0.2 mol/l KCl, respectively. The reason for choosing a glass slide was the exclusion of additional material conductance due to either porosity or swelling.

3. DISCUSSION OF RESULTS

Fig. 1 shows the dependence of the solid surface zeta potential of borosilicate glass slides on the ionic strength of KCl in aqueous solution. The zeta potential is determined from the measurements of streaming current and streaming potential, respectively, which are related by the corresponding equations of von Smoluchowski (Luxbacher 2014),

$$\zeta(I_{str}) = \frac{dI_{str}}{d\Delta p} \times \frac{\eta}{\varepsilon_0 \times \varepsilon_r} \times \frac{L}{A} \quad (1)$$

and

$$\zeta(U_{str}) = \frac{dU_{str}}{d\Delta p} \times \frac{\eta}{\varepsilon_0 \times \varepsilon_r} \times \kappa_B \quad (2)$$

where $dI_{str}/d\Delta p$ and $dU_{str}/d\Delta p$ are the streaming current and streaming potential coefficients defined as the relative changes of streaming current and potential with differential pressure. ε_0 is the permittivity in free space. ε_r , η , and κ_B are the dielectric coefficient, viscosity and electrical conductivity of water. L/A is the cell constant of the streaming channel (the rectangular gap between adjacent flat sheet membrane surfaces), i.e., the ratio of length L and cross-section A (a rectangle with width W and height H). The last term in Eq. (1) and (2), κ_B and L/A , respectively, determine the applicability of these equations for the calculation of the surface zeta potential. In the case of flat sheet membranes (as well as of the glass slide, which we use as a model surface), both equations are applicable, since we know the dimensions of the streaming channel and thus L/A as well as the electrical conductivity κ_B of the aqueous solution. However, the latter is only accepted as a substitute for the conductivity inside the streaming channel if the solid sample or the solid-liquid interface do not introduce an additional source of conductance. Ionic conductance has to be assumed for porous material such as membranes. Indeed the membrane body conductance was demonstrated to be significant and leads to an underestimation of the zeta potential calculated by Eq. (2) (Yaroshchuk 2002). As shown in Fig. 1 even the glass surface exhibits a deviation between the different approaches to the zeta potential, i.e. either

streaming current or streaming potential measurements, at low ionic strength. This deviation is assigned to interfacial conductance which is carried by the accumulation of counter-ions that compensate the surface charge, which is thus a phenomenon for all solid samples. The contribution of interfacial conductance becomes negligible at an ionic strength of 0.001 mol/l and above but must be taken into account when using the proposed approach of an extrapolation of streaming potential data obtained in the range of 10^{-6} mol/l to 0.1 mol/l for the estimation of the zeta potential at high salinity.

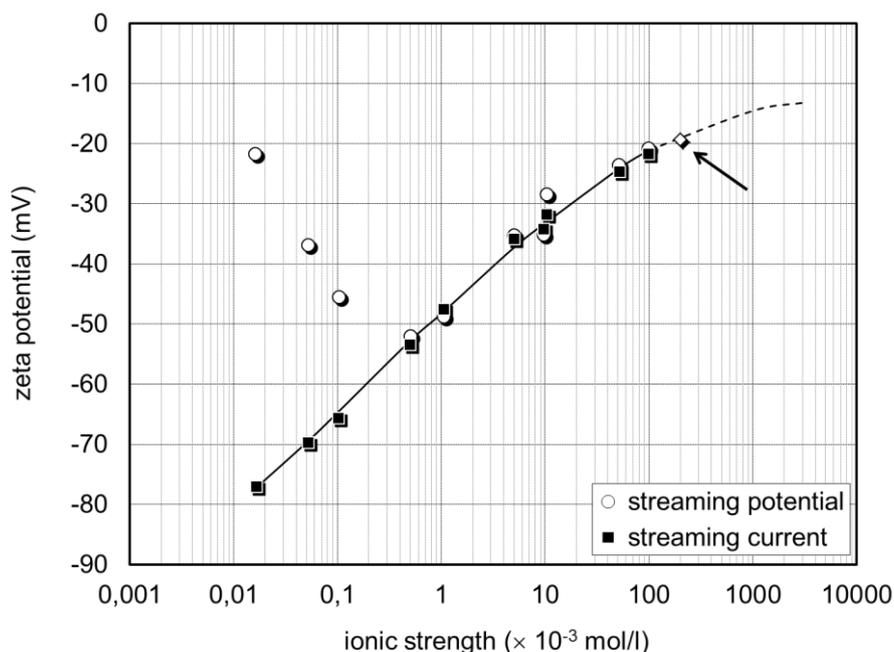


Fig. 1 Ionic strength dependence of zeta potential for a glass surface (the arrow indicates the measured zeta potential at 0.2 mol/l)

According to the model of the electrochemical double layer, which describes the charge distribution at the solid-liquid interface and defines the electrokinetic or zeta potential, the zeta potential decreases with increasing ionic strength. The explanation for this decrease is the accumulation of an increasingly higher number of counter ions that compensate the surface charge (which on the contrary increases with ionic strength due to shielding of electrostatic repulsion between neighboring surface functional groups) at a distance closer to the surface. The decline of the electrical potential at the solid-liquid interface is thus steeper and the potential at the shear plane, i.e. the zeta potential, smaller in magnitude. While the streaming current coefficient $dI_{str}/d\Delta p$ decreases in the same manner as the zeta potential (due to the linear dependence in Eq. (1)), the streaming potential coefficient $dU_{str}/d\Delta p$ decreases almost double-exponentially with increasing ionic strength. On the other hand the effect of the ionic strength on the extension of the layer of surface-charge compensating counter ions is defined by the Debye length κ^{-1} (not to mix up with the conductivity κ_B), which is proportional to $I^{-1/2}$. When plotting the logarithm of the streaming potential coefficient versus the inverse square root of ionic strength, we obtain a linear dependence. Fig. 2 shows the corresponding data for the glass surface. When extrapolating the experimental data to high salinity, e.g., 0.6 mol/l for seawater, or 3 mol/l for brackish

water proposed as an effective draw solution for forward osmosis processes, and converting the extrapolated streaming potential coefficient to zeta potential according to Eq. (2) we obtain the data indicated by the dashed line in Fig. 1. Note that at such high salinity we do not need to take membrane body conductance or even interfacial conductance into account. Fig. 1 also shows experimental data of zeta potential determined at an ionic strength of 0.2 mol/l. The experimental data matches the zeta potential predicted by the extrapolation of $dU_{str}/d\Delta p$.

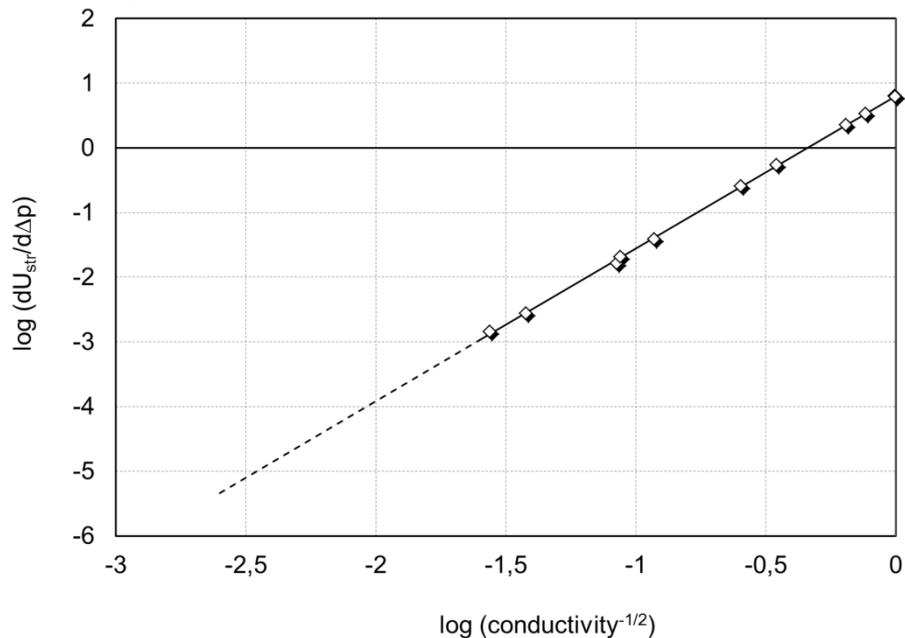


Fig 2 Dependence of streaming potential coefficient in ionic strength

When applying this procedure to the zeta potential data obtained for thin-film composite membranes for forward osmosis, we obtain the extrapolated data shown in Fig. 3. The experimental data, i.e., streaming potential and current coefficients and the corresponding zeta potential, were obtained in aqueous KCl solutions of different ionic strength (0.002, 0.015, 0.04 mol/l). As for the model surface of the glass slide, the zeta potential tends to level off at high salinity, which is unexpected from the prediction of the EDL model. The EDL model predicts that the zeta potential will vanish at high ionic strength since the surface charge gets fully compensated by counter ion accumulation within the stagnant layer and the potential thus decays to zero within this layer. However, this simple prediction does not consider the increasing density of surface charge with increasing ionic strength (due to the aforementioned decrease of the electrostatic repulsion between deprotonated functional surface groups) and the hydration of the counter ions. The latter introduces a steric hindrance and limits the accumulation of ions in the stagnant layer. In addition the thickness of this stagnant layer was estimated in the range of ionic radii at high salinity conditions (Vinogradov 2010) such that the thickness of this layer is indeed in the range of molecular dimensions.

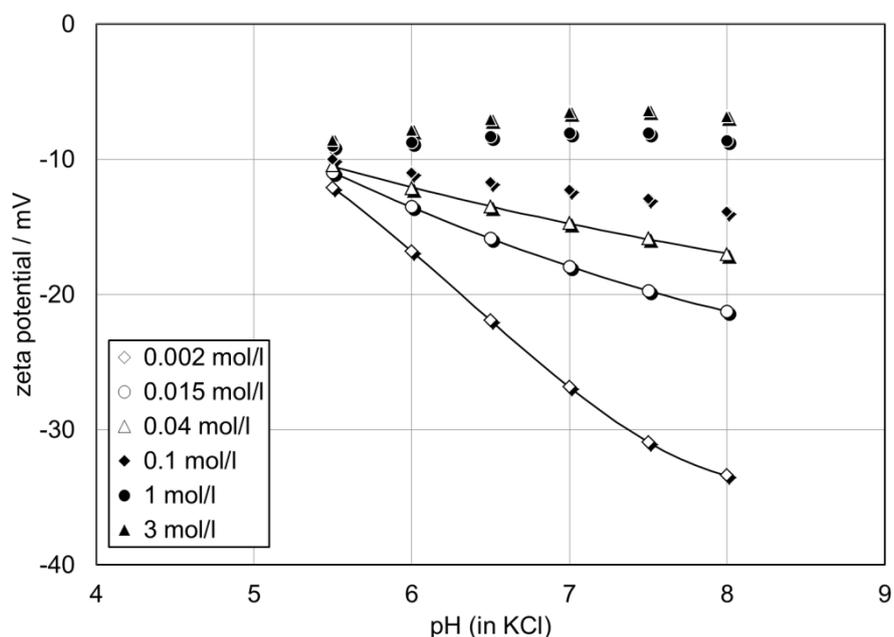


Fig 3 Measured (empty symbols) and extrapolated zeta potential (filled symbols) for membrane TFC1

It thus becomes evident that the zeta potential at the membrane-water interface approaches a finite equilibrium value under high salinity conditions. A zeta potential of $\zeta = -7$ mV at $I = 3$ mol/l is still significant. Note that this value is dependent on the membrane surface chemistry as well as on the composition of the aqueous solution. By taking into account the composition of artificial or even natural seawater, which contain i.a. divalent cations and anions that are likely to interfere with the membrane surface in a selective manner, we have to expect different zeta potential when a given membrane gets exposed to different feed waters. Although the electrostatic interaction between the membrane surface and solutes in high salinity brines is not expected to be of long range, the affinity to membrane fouling but also the partitioning of ions and other charged solutes by membranes is still determined by the surface charge. From a practical perspective the ionic strength of a complex composition of feed water at high salinity, which is not defined under such condition, may be replaced by the electrical conductivity for the estimation of the membrane zeta potential.

4. CONCLUSIONS

The attempt of the membrane zeta potential analysis at high feed water salinity is limited by the sensitivity of the streaming potential measurement under such conditions. Extrapolation of the zeta potential data obtained in the low to medium range of ionic strength towards high salinity seems feasible. However, the extrapolation to high salinity on the log scale of ionic strength will give misleading results. It does not foresee the approach of the zeta potential to a finite equilibrium value at high salinity. This equilibrium value may be reliably obtained by making use of the correlation between

the streaming potential coefficient $dU_{str}/d\Delta p$ and the Debye length that describes the extension of the diffuse layer of the EDL at the solid-liquid interface.

The analysis of streaming current and streaming potential data for forward osmosis membranes shows a significant zeta potential at an ionic strength as high as 3 mol/l which predicts that electrostatic interactions are maintained at high salinity. The suggested method for the extrapolation of zeta potential to high ionic strength enables the direct correlation between the charge density at the membrane-feed water interface with membrane properties such as salt rejection and fouling propensity.

REFERENCES

- Bellmann, C., Klinger, C., Opfermann, A., Böhme, F. and Adler, H. J. P. (2002), "Evaluation of surface modification by electrokinetic measurements", *Progr. Org. Coat.*, **44**(2), 93-98.
- Luxbacher, T. (2006), "Electrokinetic characterization of flat sheet membranes by streaming current measurement", *Desalination*, **199**(1-3), 376-377.
- Ripoll, L., Bordes, C., Marote, P., Etheve, S., Elaissari, A. and Fessi, H. (2012), "Electrokinetic properties of bare or nanoparticle-functionalized textile fabrics", *Colloids Surf., A* **397**, 24-32.
- Vinogradov, J., Jaafar, M. Z., Jackson, M. D. (2010), "Measurement of streaming potential coupling coefficient in sandstones saturated with natural and artificial brines at high salinity", *J. Geophys. Res.*, **115**, B12204:1-18
- Yaroshchuk, A., Ribitsch, V. (2002), "Role of channel wall conductance in the determination of zeta-potential from electrokinetic measurements", *Langmuir*, **18**, 2036-2038
- Zimmermann, R., Freudenberg, U., Schweiss, R., Küttner, D. and Werner, C. (2010), "Hydroxide and hydronium ion adsorption – a survey", *Curr. Opin. Colloid Interface Sci.*, **15**(3), 196-202.