Estimating the Surface Charge of a Ceramic NF Membrane

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Abstract

Determining the zeta potential for various salt types at various concentrations and pH levels was the primary goal of this effort. In order to establish a relationship between the kind and concentration of ions and the membrane's active surface charge (X_m). Using the measure zeta potential, the Gouy-Chapman equation and the simplified Grahame equation were used to estimate the membrane surface charge density (σ^s). The active surface charge (X_m) of the membrane was then determined.

Keywords: Nanofiltration, Zeta Potential

1. Introduction

In terms of pore radius, a Nanofiltration membrane falls within the range of Ultrafiltration and reverse osmosis. Nanofiltration membranes provide an ion-selective filtration medium with high flux, low operating pressure, and they are even considered as a part of the material for the membrane in a pure water system. Pore blocking and surface fouling affect the performance of Nanofiltration membranes as undesirable phenomena. The important thing is that the surface charge on the membrane decides whether or not the inorganic and organic colloidal substances attach themselves to the membrane surface when they are in an aqueous solution. It is also an important parameter to consider in Nanofiltration membranes determination of the membrane surface charge, which is associated with electro-kinetic potential, or zeta potential. A ceramic Nanofiltration membrane generates a surface charge on contact with an electrolyte solution. The distribution of ions at the solution-membrane interface is influenced by this charge; co-ions are repelled, and counter-ions are attracted to the membrane's surface charge. As a result, an electrical double layer forms on the membrane surface (Al-Alawy, et al., 2018). The bulk solution concentration determines the surface charge of the membrane. Zeta-potential, also referred to as the electro-kinetic potential, is a result of the membrane surface charge. The sign and amount of the membrane surface charge are determined by the zeta potential (Afonso, et al., 2001).

Ceramic Nanofiltration membrane charge is dependent on the complexity and concentration of the electrolyte solution to be filtered, as well as the material of the membrane. Since the majority of metal

oxides used to produce ceramic Nanofiltration membranes have an amphoteric nature, their surface electric charge is influenced by the pH of the feed electrolyte solution (Adio, et al., September 2015). The ion size that needs to be filtered should be taken into account in addition to the influence of the zeta potential, particularly if the aqueous solution contains complex cations and anion. The membrane's iso-electric point (ISP) and the pH of the solution determine the membrane charge (Hagmeyer & Gimbel, 1998).

The membrane effective surface charge and the impact of the solution pH on the membrane effective surface charge were determined in this work using electro-kinetic potential measurements. The salts NaCl, NaNO$_3$, Na$_2$SO$_4$, and MgCl$_2$ were utilized. The salt concentrations were 0.1, 0.1 and 1.0 M (Hagmeyer, et al., 1998). The used membrane was ceramic (TiO$_2$) membrane with a pore size of 1.0×10^{-9} nm (Leroy, et al., 2011).

2. Theory

The electrochemical characteristics of the ceramic membrane with respect to the charged solutes influence the ion separation process. The relative mobility of an electrolyte solute and a charged membrane surface can give rise to the membrane electro-kinetic phenomenon (Montalvillo, et al., 2011). The correlation between the membrane zeta potential and the membrane surface charge density (σ^s) can be predicted by using the simplified Grahame equation (Bhowmik, et al., 2012); which given as

$$\sigma^s = \frac{-\varepsilon\zeta}{K^{-1}} \qquad (1)$$

The Gouy-Chapman equation can be used to calculate the membrane surface charge density (σ^s) (Onimisi, et al., 2015) as follows

$$\sigma^s = \sqrt{2\varepsilon_o\varepsilon_r k_b T \sum_{i=1}^{n} c_i N_A \exp\left(\left[\frac{-z_i e\zeta}{k_b T}\right] - 1\right)} \qquad (2)$$

Because the zeta potential is related to the electrostatic repulsion between the membrane surface charge and the ion charge of the feed solution, it is utilized to calculate the membrane surface charge (Al-Alawy, et al., 2018). There are several ways to assess the membrane zeta potential, including
(a) Micro-electrophoresis method.
(b) Electro-osmosis method.
(c) Streaming potential method.

In this work, the membrane sample's zeta potential was measured using the micro-electrophoresis method after the membrane had been grinded. The approach' drawback is that the active and support layers would be combined when the membrane is grinded. Human error during the use of the other procedures is higher than the error coming from the crushed mixture. The permittivity is given as

$$\varepsilon = \varepsilon_r\varepsilon_o \qquad (3)$$

The Debye length (K^{-1}) is

$$K^{-1} = \sqrt{\frac{\varepsilon_r \varepsilon_o k_B T}{2000\, e^2\, I\, N_A}} \qquad (4)$$

The ionic strength is

$$I = \frac{\sum z_i^2 c_i}{2} \qquad (5)$$

The active membrane surface fixed charge (Xm) represents the concentration of electrically charged groups on the surface of membrane (Leroy, et al., 2011). The active membrane fixed charge can be determined by converting the membrane surface charge density (σ^s) to units of concentration (Al-Alawy, et al., 2018) as follows

$$X_m = \frac{2\sigma^s}{r_p F} \qquad (6)$$

3. Calculations and Results

Initially, four distinct types of salts were employed to determine the membrane zeta potential for ceramic nanofiltration membranes: sodium chloride (NaCl), magnesium chloride (MgCl$_2$), sodium nitrate (NaNO$_3$), and sodium sulphate (Na$_2$SO$_4$). Three distinct solutions were made for each salt, ranging in concentration from 0.01M to 1.0M (Montalvillo, et al., 2011).

The membrane was first cleaned with distilled water and allowed to dry; subsequently, it was ground into a powder. The membrane powder was then immersed in a 0.1M HCl solution for a whole day. Afterwards, distilled water was used to wash the membrane powder until its pH was neutral (Li, et al., 2015). Lastly, the previously prepared solutions were mixed with the membrane powder and allowed to settle. The zeta potential was determined using the solution's top layer. The zeta potential was measured using a zeta-sizer equipment (zeta-sizer 300HS advance, laser Doppler velocimeter).

The membrane's zeta potential values were positive when MgCl$_2$ and NaNO$_3$ solutions were utilized (Danielewicz-Ferchmina, et al., 2004). When the Na$_2$SO$_4$ solution had been used, it had negative zeta potential values. However, when the NaCl solution had been used, the membrane showed positive zeta potential values for the 0.1M and 1.0M solutions, but a negative value for the 0.01M concentration solution (Li, et al., 2004).

Permittivities are measured following the measurement of the membrane zeta potential (Bhowmik, et al., 2012). Equations (4) and (5) were utilized to determine the Debye length (K^{-1}) for the salts that were used as follows

o   For 1:1 electrolyte (NaCl)

$$K^{-1} = \left(3.432 \times 10^{-11}\right)\sqrt{\frac{\varepsilon_r}{c_{NaCl}}}$$

o   For 1:1 electrolyte (NaNO$_3$)

$$K^{-1} = \left(3.432 \times 10^{-11}\right)\sqrt{\frac{\varepsilon_r}{c_{NaNO_3}}}$$

o   For 1:2 electrolyte (Na$_2$SO$_4$)

$$K^{-1} = \left(3.432 \times 10^{-11}\right)\sqrt{\frac{\varepsilon_r}{\left(\frac{5}{2}\right)c_{Na_2SO_4}}}$$

o   For 2:1 electrolyte (MgCl$_2$)

$$K^{-1} = \left(3.432 \times 10^{-11}\right)\sqrt{\frac{\varepsilon_r}{\left(\frac{5}{2}\right)c_{MgCl_2}}}$$

Table (1) displayed the Debye length and zeta potential results. Equations (1) and (2) were used to get the membrane surface charge density (σ_s) using the simplified Grahame equation and the Gouy-Chapman equation, respectively. The tables (2), (3), and (4) displayed the results. Next, using equation (6), the active membrane fixed charge (X_m) was determined. It was observed that the active membrane surface charge (X_m) findings differed between the Simplified Grahame equation and the Gouy-Chapman equation.

According to Figure 2, there were only positive charge values for the active membrane surface charge when the Gouy-Chapman equation was applied. Nevertheless, the zeta potential is in agreement with the simplified Grahame equation, which had both positive and negative values (Figure 1). A positive active membrane surface fixed charge (X_m) was the only feature of the membrane for Na$_2$SO$_4$ solution (Li, et al., 2015).

In contrast, the active membrane surface fixed charge for NaNO$_3$ and MgCl$_2$ was negative. However, in the NaCl situation, the iso-electric point (ISP) would be at a concentration value of 4e2 mol/m^3. The surface fixed charge of the active membrane did change from a positive to a negative value. Furthermore, for the different salts and concentrations, the active membrane surface charge increased and the membrane zeta potential dropped with increasing salt concentration (Figures 1 and 3).

According to the Gouy-Chapman equation, the membrane surface charge increased as the concentration of salts increased. Figure 2 shows that whereas the membrane charges of NaCl, MgCl$_2$, and NaNO$_3$ were comparable, the membrane surface charges of Na$_2$SO$_4$ were greater. The membrane surface charges for the two methods were comparable in the case of Na$_2$SO$_4$.
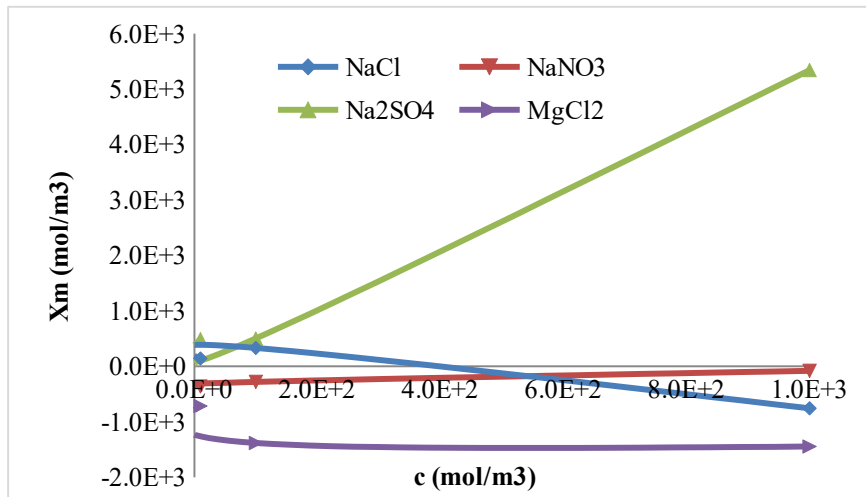
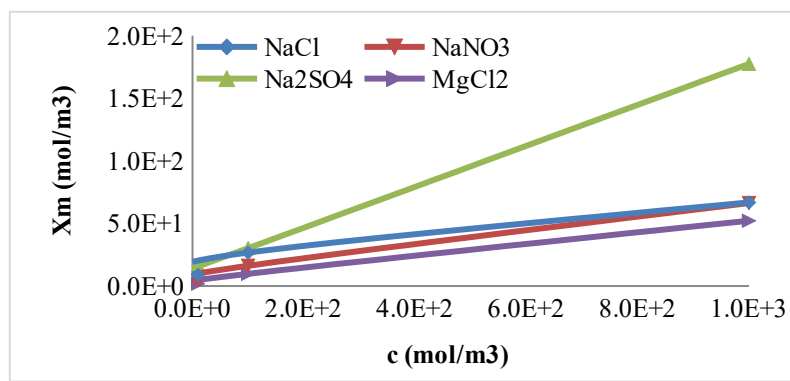Figure 1: Active Membrane Surface Charge versus Ion Concentration (Simplified Grahame Equation)

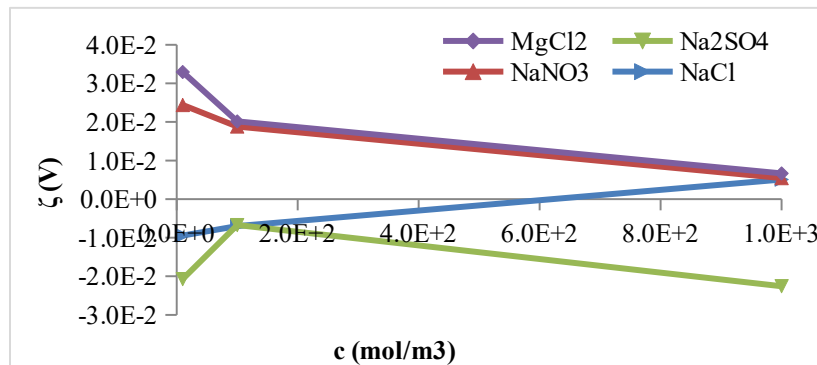Figure 2. Active Membrane Surface Charge versus Ion Concentration (Gouy-Chapman Equation)

Figure 3: ζ versus c

It was also observed that the active membrane surface charge (X_m) values differed between the Gouy-Chapman equation and the simplified Grahame equation in the case of NaCl solution at pH ranging between 3 and 10 (Zayid, 2014). In contrast to the Gouy-Chapman equation, which only had positive surface charge values, the simplified Grahame equation featured both positive and negative surface charge values. In the case of the simplified Grahame equation; the active membrane charge changed from positive to negative around pH 5, which is similar to zeta potential results (Figures 4 and 6).

Figures 4 and 5 show that for both approaches - the Gouy-Chapman equation and the simplified Grahame equation- the active membrane charge increased as the pH and NaCl concentration increased.

Figure 5 illustrates how the concentration of NaCl had a more pronounced effect on the active membrane surface charge in the Gouy-Chapman equation.

Figure 6 shows that the zeta potential value for the 10 mol/m^3 solution was higher than the 100 mol/m^3 solution. However, compared to 10 mol/m^3 solution, the active membrane surface charge of 100 for mol/m^3 solution was larger (Figures 4 and 5) (Zayid, 2014). It was observed from the active membrane surface fixed charge and pH relation that the iso-electric point (ISP) shifted at pH values of 5 and below. The relationship between pH and zeta-potential (Figure 6) supports this (Bhowmik, et al., 2012). Figure 4 shows the shift in the active membrane surface fixed charge from negative to positive. However, at pH 5 (Figure 6), the zeta-potential values shifted from positive to negative values (Hagmeyer & Gimbel, 1998).
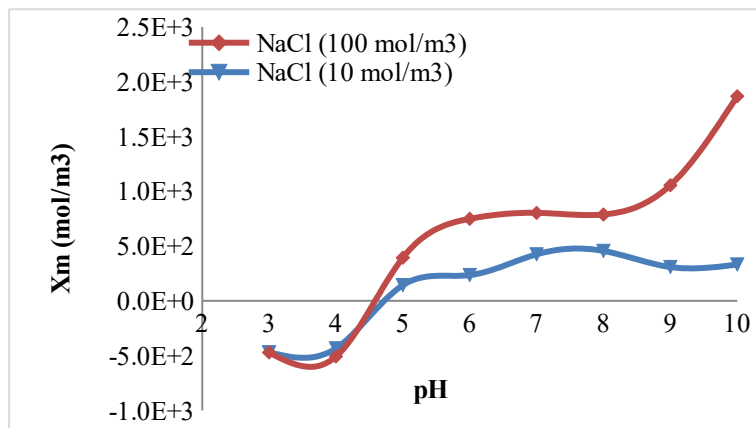

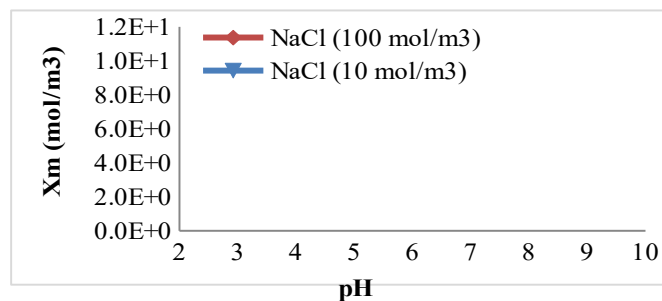Figure 4: Active Membrane Surface Charge versus pH (Simplified Grahame Equation)

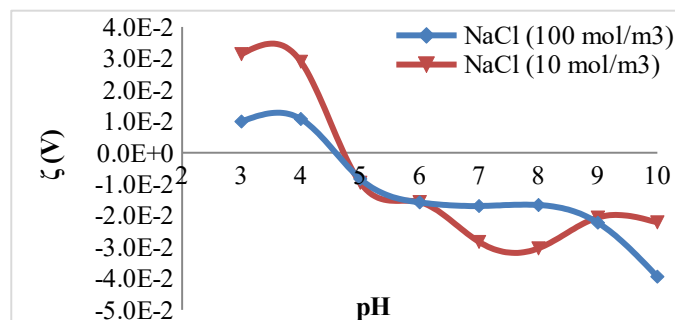Figure 5: Active Membrane Surface Charge versus pH (Gouy-Chapman Equation)

Figure 6: Zeta Potential versus pH

4. Conclusion

This work aimed to compute the surface fixed charge of the active membrane using the zeta poetical for several salt types at various concentrations and pH levels. The type and concentration of the salt were shown to have an impact on the membrane zeta potential. Therefore, the membrane surface active charge was influenced by the salt type and concentration. thus as the pH and concentration of the fluid increased so did the surface fixed charge of the active membrane (Li, et al., 2004). Accordingly the active membrane surface fixed charge would therefore impact the membrane rejection (Al-Alawy, et al., 2018).

Attraction between anions like Cl^{1-}, SO_4^{2-}, and NO_3^{1-} and the membrane active surface charge would happen if the membrane active surface charge was negative. Consequently, the membrane's rejection of the anions would increase and not allowing the anions to pass through the permeate side of the membrane. Since the membrane's positive active surface charge repelled cations like Na1+ and Mg2+, the cations were not more likely to be rejected by it and could therefore pass through to the permeate side of the membrane.

Repulsion between the membrane active surface charge and cations would happen if the membrane active surface charge was positive. As a result, there would be less rejection of cations and more rejection of anions (Hagmeyer & Gimbel, 1999).

5. Nomenclature

c_i ion concentration (mol/m^3).

e   electron charge (1.60222×10^{-19} C).

F   Faraday constant (964867 C/mol).

I   ionic strength.

k_B Boltzmann constant (1.38×10^{-23} J/K).

K^{-1} Debye length (m).

N_A Avogadro's number (6.02×10^{23} mol^{-1}).

r_p membrane pore radius (m).

T   absolute temperature (K).

X_m active membrane surface fixed charge (mol/m^3).

z_i valance of ion (i).

σ^s membrane surface charge density (C/m^2).

ε permittivity (C/V.m).

ζ zeta potential (V).

6. References

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7. Appendix-1

The NaCl relative permittivity as a function of temperature is calculated by the semi-empirical equations presented by G. R. Olhoeft (Revil, et al., September 10, 1999) as follows

(a) 273 K ≤ T ≤ 373 K

$$\varepsilon_r = a_0 + a_1 T + a_2 T^2 + a_3 T^3$$

where T is the temperature in Kelvin, a_0 is 295.68, a_1 is -1.2283 K^{-1}, a_2 is -2.094x10^{-3} K^{-2}, a_3 is -1.41x10^{-6} K^{-3}.

(b) 373 K ≤ T ≤ 643 K

$$\varepsilon_r = \frac{b_0}{T} + b_1 + b_2 T + b_3 T^2 + b_4 T^3$$

where b_0 is 5321, b_1 is -233.76 K^{-1}, b_2 is -0.9397 K^{-2}, b_3 is 1.417x10^{-3} K^{-3}, b_4 is -8.292x10^{-7}.

(c) The relative permittivity as a function of the concentration is

(d)

$$\varepsilon_r = \varepsilon_r(T) + c_1 C_f + c_2 C_f^2 + c_3 C_f^3$$

where C is the salt concentration (mol/L), c_1 is -13.0 L/mol, c_2 is -1.065 L^2/mol^2, c_3 is -0.03006 L^3/mol^3.

8. Appendix-2

Salt Type	c (mol/m³)	ζ (mV)	Conductivity (mS)	K⁻¹ (m)	ε (C/V.m)
NaCl	1.0E+01	-9.44	0.94	9.61E-11	6.94E-10
	1.0E+02	-6.99	7.33	3.04E-11	6.94E-10
	1.0E+03	5.064	35.22	9.61E-12	6.94E-10
NaNO₃	1.0E+01	24.38	1.33	9.61E-11	6.94E-10
	1.0E+02	18.8	10.25	9.61E-11	6.94E-10
	1.0E+03	5.43	30.8	9.61E-11	6.94E-10
Na₂SO₄	1.0E+01	-20.72	2.62	6.08E-11	6.94E-10
	1.0E+02	-6.72	15.64	1.92E-11	6.94E-10
	1.0E+03	-22.57	36.23	6.08E-12	6.94E-10
MgCl₂	1.0E+01	32.94	2.32	5.58E-11	5.84E-10
	1.0E+02	20.14	16.98	1.76E-11	5.84E-10
	1.0E+03	6.663	44.86	5.58E-12	5.84E-10

Table 1: Zeta Potential, Debye Length

Salt Type	c (mol/m³)	σ^s (C) (Simplified Grahame Equation)	X_m (mol/m³) (Simplified Grahame Equation)	σ^s (C) (Gouy-Chapman Equation)	X_m (mol/m³) (Gouy-Chapman Equation)
NaCl	1.0E+01	6.82E-02	1.41E+02	4.27E-03	8.86E+00
	1.0E+02	1.60E-01	3.31E+02	1.29E-02	2.67E+01
	1.0E+03	-3.66E-01	-7.58E+02	3.22E-02	6.68E+01
NaNO₃	1.0E+01	-1.76E-01	-3.65E+02	2.21E-03	4.59E+00
	1.0E+02	-1.36E-01	-2.81E+02	7.80E-03	1.62E+01
	1.0E+03	-3.92E-02	-8.13E+01	3.20E-02	6.63E+01
Na₂SO₄	1.0E+01	2.37E-01	4.90E+02	7.97E-03	1.65E+01
	1.0E+02	2.43E-01	5.03E+02	1.46E-02	3.03E+01
	1.0E+03	2.58E+00	5.34E+03	8.56E-02	1.78E+02
MgCl₂	1.0E+01	-3.45E-01	-7.16E+02	9.05E-04	1.88E+00
	1.0E+02	-6.67E-01	-1.38E+03	4.71E-03	9.76E+00
	1.0E+03	-6.98E-01	-1.45E+03	2.52E-02	5.22E+01

Table 2: σ^s and X_m

Salt Type	pH	K⁻¹ (m)	σ^s (C) (Simplified Grahame Equation)	X_m (mol/m³) (Simplified Grahame Equation)	ε (C/V.m)	σ^s (C) (Gouy-Chapman Equation)	X_m (mol/m³) (Gouy-Chapman Equation)
NaCl (10 mol/m³)	3.00E+00	9.61E-11	-2.26E-01	-4.69E+02	6.94E-10	1.93E-03	4.00E+00
	4.00E+00	9.61E-11	-2.09E-01	-4.34E+02	6.94E-10	2.02E-03	4.19E+00
	5.00E+00	9.61E-11	6.92E-02	1.43E+02	6.94E-10	4.29E-03	8.88E+00
	6.00E+00	9.61E-11	1.14E-01	2.35E+02	6.94E-10	4.83E-03	1.00E+01
	7.00E+00	9.61E-11	2.05E-01	4.25E+02	6.94E-10	6.18E-03	1.28E+01
	8.00E+00	9.61E-11	2.20E-01	4.56E+02	6.94E-10	6.43E-03	1.33E+01

| | 9.00E+00 | 9.61E-11 | 1.49E-01 | 3.09E+02 | 6.94E-10 | 5.31E-03 | 1.10E+01 |
| | 1.00E+01 | 9.61E-11 | 1.60E-01 | 3.32E+02 | 6.94E-10 | 5.48E-03 | 1.14E+01 |

Table 3: σ^s and X_m at 10 mol/m^3 Nacl

Salt Type	pH	K^{-1} (m)	σ^s (C) Simplified Grahame Equation	X_m (mol/m^3) (Simplified Grahame Equation)	ε (C/V.m)	σ^s (C) (Gouy-Chapman Equation)	X_m (mol/m^3) (Gouy-Chapman Equation)
NaCl (100 mol/m^3)	3.00E+00	3.04E-11	-2.27E-01	-4.70E+02	6.94E-10	9.27E-03	1.92E+01
	4.00E+00	3.04E-11	-2.45E-01	-5.07E+02	6.94E-10	9.13E-03	1.89E+01
	5.00E+00	3.04E-11	1.90E-01	3.94E+02	6.94E-10	1.32E-02	2.74E+01
	6.00E+00	3.04E-11	3.61E-01	7.49E+02	6.94E-10	1.53E-02	3.17E+01
	7.00E+00	3.04E-11	3.88E-01	8.03E+02	6.94E-10	1.57E-02	3.24E+01
	8.00E+00	3.04E-11	3.80E-01	7.88E+02	6.94E-10	1.56E-02	3.22E+01
	9.00E+00	3.04E-11	5.09E-01	1.05E+03	6.94E-10	1.74E-02	3.60E+01
	1.00E+01	3.04E-11	9.01E-01	1.87E+03	6.94E-10	2.42E-02	5.03E+01

Table 4: σ^s and X_m at 100 mol/m^3 Nacl