

## Characterizations of Membrane for Water Treatment: Surface Charge Analysis by Electrophoresis and Acidity Measurements

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**Abstract :** The surface charge properties of a polymeric NF and a ceramic UF membranes were characterized in terms of zeta potential and acidity. Both the negative zeta potential and acidity values increased as pH increases due to ionizable acidic functional groups. Increased ionic strength reduced the acidity of the negatively-charged membrane surface as anticipated. Through these results, it can be envisioned that the electrostatic interaction can play an important role when negatively-charged membranes are used to reject solutes with ionizable functional groups. Fouling of the negatively-charged membrane with natural organic matter (NOM) having a negative charge density was also investigated with respect to the surface charge. The surface charge of the NF membrane increased negatively when greater NOM adsorption onto the membrane surface occurred.

### 1. Introduction

Membrane process is one of promising advanced water treatments in the aspects of removing disinfection by-products (DBPs) precursor (natural organic matter (NOM)) and pathogenic microorganisms. There are two membranes that can be used for membrane filtration processes; polymeric membranes exhibit relatively high permeability, while, ceramic (inorganic) membranes can have comparatively high resistance to severe chemical environments. The performance of both membranes may substantially be reduced when they experience fouling phenomena induced by severe concentration polarization and adsorption of potential foulant solutes.

There are two major mechanisms in membrane application for solute rejection: size exclusion and electrostatic interaction [1]. The pH and ionic strength of a solution can influence these solute-rejection mechanisms by changing pore size and

surface charge of a membrane. Moreover, the interactions between foulants and the membrane surface (or pores) may alter the membrane performance in terms of solute rejection, thus, it should be investigated rigorously and collectively.

In this paper, we attempted to investigate the membrane surface charge using zeta potential and acidity measurements under different pH and ionic strength (I) conditions. The zeta potential can be determined by the streaming potential and electrophoresis measurement methods [2]. It can be hypothesized that the membrane surface charge increases negatively with increasing pH due to ionizable functional groups and decreases negatively with higher ionic strength due to the compaction of the double layer. For a membrane containing the iso-electric point of below 6, for example, NOM included in natural waters with the pH range between pH 6 and 8 can be anticipated to be effectively removed due to the charge repulsion between NOM acids and the

negative-charged membrane surface. Different ionic strength conditions can modify the membrane surface charge, providing substantial changes in solute rejection.

## 2. Methods and Materials

### 2.1. Zeta Potential Measurement

Even though the membrane surface and colloids (or particles) contain charge related properties, the surface charge can not be measured directly. Thus, the zeta potential (in unit of mV) is used as an indicator of the surface charge. The zeta potential may be defined as the potential on the shear plane which is located between the fixed layer and the diffusion layer. A commercialized electrophoresis measurement apparatus (ELS-8000, Otsuka Electronics, Japan) was used to measure electromobility and corresponding zeta potential value. As a standard particle, polystyrene latex (size of 520 nm) was used, and the standard particles were coated by hydroxy propyl cellulose (HPC) to prevent the interactions and adsorption with the measurement quartz cell surface. The particles were dispersed in a 10mM NaCl solution.

Two different (a polymeric nanofiltration (NF) and a ceramic (titania) ultrafiltration (UF)) membranes were examined for this study: ESNA (polyamide NF, MWCO=250 mass units, Hydronautics, U.S) and T-1000 (titania UF, MWCO=1000 mass units, TAMI, France).

### 2.2. Functionality Analysis by Acidic Titration

The charge density in terms of carboxylic and phenolic groups was determined using a micro titrator (Metrohm, CH-9101). Consumed amount of 0.05N NaOH was used to calculate the acidity in the unit of meq/g-dried membrane. The effects of ionic strength and divalent cation presence were also evaluated with additions of NaCl and  $Ca^{2+}$ , respectively.

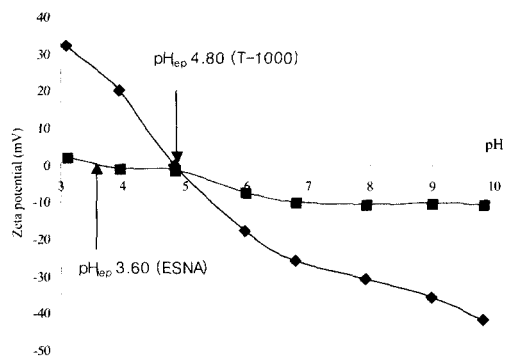


Fig. 1. Zeta potential values of ESNA and T-1000 membranes.

## 3. Results and Discussion

### 3.1. Iso-electric Point (i.e.p.) of Polymeric/Ceramic Membranes

The iso-electric point was obtained by plotting the measured zeta potentials as a function of pH. Figure 1 shows that the i.e.p. of the NF membrane is somewhat smaller than that of the UF. The NF and UF membranes exhibit negative charge in the pH range above 3.60 and 4.80 (i.e., i.e.p.), respectively, suggesting that negative-charged solutes (for example, NOM acids and haloacetic acids) can be effectively rejected by the negatively-charged membrane surface, which is due to the charge interaction mechanism.

### 3.2. Functionality Analyses of Polymeric and Ceramic Membranes.

Figures 2 and 3 represent the acidity trends (meq/g-dried membrane) of the NF and UF membranes under different ionic strength conditions. When there is no ionic strength adjustment, the acidity trends of both the NF and UF membranes are comparatively similar (NF: 0.057 vs. UF: 0.058). However, at a higher ionic strength (adjusted by NaCl), the acidities of the NF membrane decreased more significantly than the UF membrane (NF: 0.028 vs. UF: 0.045). Thus, the levels of surface charge of the NF membrane seem to be reduced by the double layer compaction which was resulted from increased ionic strength. On

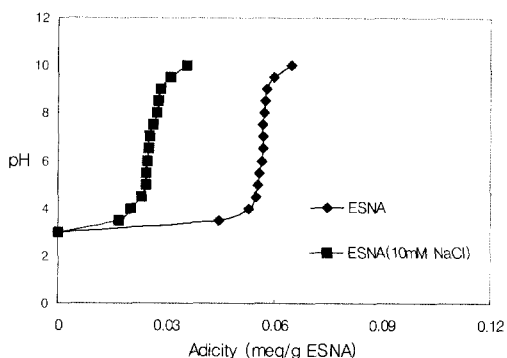


Fig. 2. Ionic strength effect on the acidity of the NF membrane.

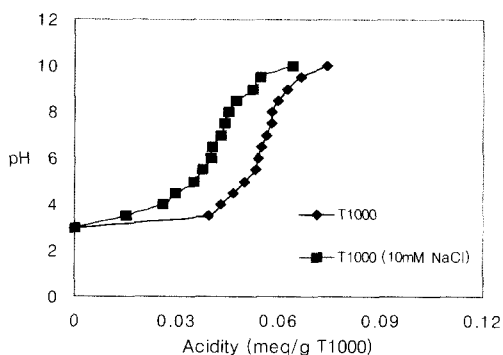


Fig. 3. Ionic strength effect on the acidity of the UF membrane.

the other hand, the UF membrane appears to be influenced by increase in ionic strength. We believe that this result is attributed to the material stiffness which can not be compacted or expanded under different conditions.

### 3.3. The Effects of NOM Fouling on the Surface charge

To evaluate the effects of NOM fouling on the surface charge in terms of zeta potential, clean NF membrane was soaked into NOM solutions with different concentrations ranging 10–500 mg/L for 7 days. The zeta potential variations of clean and NOM-fouled membranes were depicted in Figure 4 over a pH range of 3–9. The zeta potential values of the examined NF membranes appear not to decrease in a pH range above approximate 6. Almost all of ionizable functional

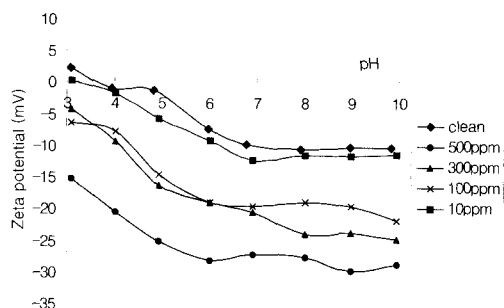


Fig. 4. pH dependence of zeta potential determined by electromobility measurement for the NF membrane soaked in NOM solutions with different concentrations.

groups which provide the negative surface charge seem to be deprotonated at the pH of approximate 6.0, with the ionizable functional groups from either adsorbed NOM molecules (i.e., NOM acids) or polymeric structure of the membrane surface. The zeta potential values of the NOM-fouled membrane were negatively higher than clean membrane because the adsorbed NOM contains acidic functional groups with higher charge density than membrane polymer itself (see Figure 4). The higher NOM concentration, the negatively-higher zeta potential values were shown.

## 4. Summary and Conclusions

Many useful information on the membrane surface in terms of zeta potential and surface functionality could be obtained using electrophoresis and acidity measurements. The effects of pH and ionic strength on the surface charge were also demonstrated. Through the zeta potential and acidity measurements with the examined membranes, charge interactions between the negatively-charged membrane surface and solutes with ionizable functional groups can be hypothesized to be an influencing mechanism for membrane performance. More rigorous characterizations of the membrane surface are to be evaluated in terms of zeta potential, functional groups analysis (by FTIR for carboxylic and phenolic groups), and pore size distribution (by solute rejection and

AFM methods).

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## References

1. J. Cho, G. L. Amy, and J. Pellegrino, *J. Membrane Sci.* **164**, 89 (2000).
2. M. Elimelech, W. H. Chen, and J. J. Waypa, *Desalination*, **95**, 269 (1994).