



# Surface charge characterization of nanofiltration membranes by potentiometric titrations and electrophoresis: Functionality vs. zeta potential



Hojung Rho<sup>a</sup>, Kangmin Chon<sup>b,\*</sup>, Jaeweon Cho<sup>a,\*</sup>

<sup>a</sup> School of Urban and Environmental Engineering, Ulsan National Institute of Science and Technology (UNIST), 50 UNIST-gil, Eonyang-eup, Ulsju-gun, Ulsan 44919, Republic of Korea

<sup>b</sup> Department of Environmental Engineering, College of Engineering, Kangwon National University, 1 Kangwondaehak-gil, Chuncheon-si, Gangwon-do 24341, Republic of Korea

## ARTICLE INFO

### Keywords:

Functionality  
Point of zero charge  
Surface charge  
Titration  
Zeta potential

## ABSTRACT

The surface charge properties (i.e., functionality and zeta ( $\zeta$ ) potential) of two nanofiltration (NF) membranes were characterized by potentiometric titrations and electrophoresis to predict the electrostatic transport at the membrane surfaces affecting their salt rejection and fouling propensities. The  $\zeta$  potential was not suitable for evaluating the rejection of  $\text{Na}^+$  (NE20 membrane = 21–25%; NE70 membrane = 65–70%) and  $\text{Cl}^-$  ions (NE20 membrane = 19–22%; NE70 membrane = 60–63%), and the fouling propensities of organic materials in the NF membranes due to its inherent measurement inaccuracies ( $\Delta \zeta$  potential =  $-1.8 \times (\Delta$  amount of desorbed organic foulants) + 45.9,  $R^2 = 0.07$ ). The functionality accurately predicted both the rejection of NaCl and the fouling propensities of the organic materials, as the charge densities of the membranes determined by the functionality measurements (only TFC membranes are applicable) truly reflected the acid dissociation constants of the carboxylic and amine functional groups and the points of zero charge values. These results indicate that potentiometric titrations may provide valuable insights into the electrostatic transport at the membrane surface influencing the salt rejection and fouling mechanisms of the NF membranes.

## 1. Introduction

During recent decades, great progress has been made in the field of membrane technologies, which has enabled their use in practical applications, including drinking water production, wastewater treatment, seawater desalination, and energy recovery [1–4]. However, the efficient operation of membrane processes is still hindered by membrane fouling, which significantly influences their performance in terms of salt rejection and permeate flux decline [5]. Indeed, the surface charge properties of the membranes are considered as key factors affecting their salt rejection and permeate flux decline. For example, electrostatic interactions between charged solutes and membrane surfaces (known as Donnan exclusion) can have a significant effect on the salt rejection [6–8]. Furthermore, membrane electrostatically repel charged organic materials, colloids, and particles due to their charged surfaces at neutral pH values, which ultimately plays a critical role in the accumulation of foulants on the membrane surfaces which is associated with the decline of permeate flux [9–11]. To address these issues, many researchers have investigated the surface charge properties of membranes and their

relationship to the electrostatic transport at the surfaces, which in turn determines their salt rejection and fouling mechanisms [12–15].

The surface charge properties of membranes in contact with aqueous media are induced by the ionization of surface functional groups (e.g.,  $-\text{COOH}$ ,  $-\text{NH}_2$ , and  $-\text{SO}_3\text{H}$ ) as indicated below [16–20]:



Therefore, the  $\zeta$  (zeta) potential of the membrane surface, as determined by electrokinetic measurements, has been widely used as a surrogate parameter to represent the surface charge properties of membranes, as it theoretically corresponds to the electric potential at the shear plane between the Stern and diffuse layers, according to the electrical double layer theory [12]. However, the  $\zeta$  potential cannot accurately represent the surface charge properties of the membranes due to the distance between the surface and the shear plane of the electrical double layer. Hence, the  $\zeta$  potential is typically lower than the

\* Corresponding authors.

E-mail addresses: [kmchon@kangwon.ac.kr](mailto:kmchon@kangwon.ac.kr) (K. Chon), [jaeweoncho@unist.ac.kr](mailto:jaeweoncho@unist.ac.kr) (J. Cho).

local surface potential calculated using the diffuse double layer theory (Fig. S1, Supplementary information (SI)) [21]. In addition, the accurate measurements of  $\zeta$  potential values can be hindered by cation species in the electrolyte solutions entering the diffuse layer, as electrokinetic measurements generally employ electrolytes (e.g., NaCl or KCl) with a streaming potential to drive the pressure or electrophoretic mobility of particles [12,22–26].

To overcome these limitations, an approach capable of accurately representing the surface charge properties of the membranes is required. In this context, potentiometric titration analysis is a well-established method to quantify the ionized functional groups present in organic materials [27]. Therefore, potentiometric titrations have been employed to evaluate the complexation of natural organic matter (NOM) with heavy metals and other minerals [28–30]. As positively charged ions and particles have been found to readily complex with NOM, the electrostatic repulsion between NOM and membrane surfaces that influences membrane fouling could also be estimated using potentiometric titrations [31]. Although some studies have investigated the differences in the surface charge properties of the membranes determined by potentiometric titrations and electrophoresis, the potentiometric titration method has not yet been applied to estimate the surface charge properties of membranes and subsequent prediction of the performance of membrane processes [26,32].

The main purpose of this study was to validate a potentiometric titration method based on the quantification of ionized functional groups (termed as functionality) to estimate the surface charge properties of nanofiltration (NF) membranes. Therefore, the functionality and  $\zeta$  potential were rigorously characterized using potentiometric titrations and electrophoresis at various pH and ionic strength conditions, and directly correlated to the performance of the NF membranes in terms of salt rejection and fouling propensity.

## 2. Materials and methods

### 2.1. Physicochemical properties of the NF membranes

Two different types of thin-film composite (TFC) NF membranes, namely NE20 (nominal molecular weight cut-off (MWCO) = 1000 Da) and NE70 (nominal MWCO = 350 Da) (Toray Chemical, Seoul, Republic of Korea), were employed to compare their functionality and  $\zeta$  potential measurements. The physicochemical properties of the selected NF membranes are listed in Table 1. Although both membranes contain piperazine-based polyamides, their pore sizes in relation to the polymer-linking structures differed significantly from one another [26]. Prior to all experiments, the virgin NF membranes were soaked in deionized (DI) water for 1 day to remove the coating materials from the membrane surfaces. The functional group compositions of the NF membranes were identified using attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopy (Vertex70, Bruker, MA, USA) utilizing a ZnSe crystal at an incident angle of 45° over a scanning wavelength of 550–1800  $\text{cm}^{-1}$  with a resolution of 0.4  $\text{cm}^{-1}$  [33].

### 2.2. Surface charge characterization of the membranes using electrophoresis

The  $\zeta$  potential values of the NF membranes were measured by

**Table 1**  
The physicochemical properties of the NF membranes.

Classification	NF	
Membrane code	NE20	NE70
Manufacturer	Toray Chemical Korea Inc., Seoul, Republic of Korea	
Membrane type	Thin-film composite	
Membrane materials	Polyamide	
Water soluble monomer	Piperazine	
Nominal MWCO (Da)	1000	350

electrophoresis in a quartz cell. Due to the accumulation of cations in the electrolyte solution on the membrane surface, an asymmetric electroosmotic flow occurs through the membrane surface, which allows the monitoring particles to pass through the electrophoresis chamber. The  $\zeta$  potential values of the NF membranes can therefore be calculated from the electrophoretic mobility of the monitoring particles using the Smoluchowski equation [24,34]:

$$\zeta = 4\pi\eta U/\varepsilon_r\varepsilon_0 \quad (4)$$

where  $\zeta$  is the  $\zeta$  potential measured by electrophoresis (mV),  $U$  is the electrophoretic mobility of a monitoring particle ( $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ ),  $\eta$  is the liquid medium viscosity ( $0.89 \times 10^{-3} \text{ Pa s}$ ),  $\varepsilon_r$  is the liquid medium permittivity (78.38), and  $\varepsilon_0$  is the vacuum permittivity ( $8.854 \times 10^{-12} \text{ s m}^{-1}$ ). In this study, the  $\zeta$  potential values of the NF membranes were determined using a commercial electrophoresis analyzer (ELSZ-2000, Otsuka Electronics, Osaka, Japan) with polystyrene latex particles (diameter = 520 nm) coated with hydroxypropyl cellulose (HPC, molecular weight (MW) = 300,000 Da) as a mobility monitoring particle.

As the  $\zeta$  potential values of membranes vary significantly depending on the pH and ionic strength of the solution, the effects of pH on the  $\zeta$  potential measurements were identified using a 10.0 mM NaCl solution between pH 2.0 and 11.0. In addition, the dependence of the  $\zeta$  potential values on ionic strength at each pH (pH = 2.0, 4.0, 5.5, 7.0, 9.0, and 11.0) was investigated under 4 different ionic strength conditions (NaCl concentrations = 0.1, 1, 5, and 10.0 mM). The pH of each sample was adjusted using 0.1 M of NaOH and HCl solutions and then its  $\zeta$  potential values were subsequently measured using the electrophoresis method in 30 s. For all experiments, the electrophoresis cell constant was calibrated using a 10.0 mM NaCl solution and was used to compare the relative  $\zeta$  potential values under different ionic strength conditions, as the electric field intensity, which is closely associated with the electrophoresis cell constant, varied significantly according to the ionic strength of the electrolyte solution.

### 2.3. Surface charge characterization of the membranes using potentiometric titrations

Prior to carrying out functionality measurements using potentiometric titrations, the supporting layer was completely detached from each NF membrane coupon (only TFC membranes are applicable) and the membrane coupons were soaked in DI water for 1 d (active surface area =  $0.0031 \pm 0.0002 \text{ m}^2$ ). The soaked membrane coupons were cut into small pieces ( $\sim 1.5 \text{ mm} \times 1.5 \text{ mm}$ ) and then immersed in a 10 mM NaCl solution (40 mL). The pH of the solution was adjusted to 2.0 using 0.1 M HCl solution and the solution was titrated from pH 2.0 to 11.0 using an automatic microtitrator (702 SM, Metrohm, Herisau, Switzerland) with a 0.5 N NaOH solution to quantify the ionized carboxylic and amine functional groups present on the active layers. Although the back side of the active layer contained dibenzyl sulfone moieties, these groups did not influence the functionality measurements of the membranes as their acid dissociation constant ( $\text{p}K_a \approx 23.9$ ) is significantly higher than the pH values of the tested electrolyte solutions (pH = 2.0–11.0) [35]. After subtracting the background functionality of DI water from the titration curves, the membrane functionalities were determined as follows:

$$\text{Membrane functionality (meq/m}^2\text{membrane)} = \frac{(V_a - V_b) \times C_s}{A} \quad (5)$$

where  $V_a$  is the volume of NaOH solution consumed during titration of the active layer (mL),  $V_b$  is the NaOH volume consumed in a blank test with DI water (mL),  $C_s$  is the concentration of NaOH (N), and  $A$  is the surface area of the active layer ( $\text{m}^2$ ).

The point of zero charge (PZC) determined at the pH value where the functionality of the membrane is independent on the ionic strength is defined as the point of zero salt effect in the titration curves.

Download English Version:

<https://daneshyari.com/en/article/7008114>

Download Persian Version:

<https://daneshyari.com/article/7008114>

[Daneshyari.com](https://daneshyari.com)