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Correlation of surface concentration polarization with the surface electrochemistry of a permselective Membrane: An *ex situ* electrical impedance spectroscopy study

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ABSTRACT

Surface concentration polarization induces fouling processes accompanied by changes in the resistance of a semipermeable membrane, but the connection between these two phenomena has not yet been evaluated. Here, we propose to connect them by introducing the concept of pH equivalent (pHeq), which is used to describe the electrical properties of a polarized membrane surface in terms of a pH value at which a membrane is conditioned. First, the resistance and capacitance of polyamide thin-film membranes conditioned at different pH were evaluated *ex situ* using electrical impedance spectroscopy (EIS), which decreases and increases in proportion with increasing pH when the pH exceeds the pKa of the ionization of carboxyl groups. Filtration of 0.1 mM Fe(III) chloride solution in dead-end mode was then conducted as a model reaction for the fouling process. The occurrence of concentration polarization in the early stage indeed led the capacitance and the resistance at the membrane/electrolyte interface to a pHeq similar to that of an alkaline-like environment, while no significant decline in flux or rejection was observed. In addition to being responsible for the formation of $Fe(OH)_3$ in fouling, this high pHeq is also likely the bridge connecting the electrical characteristics of the membrane to macroscopic observations (flux and rejection) based on the electroviscous consideration.

1. Introduction

Concentration polarization is a phenomenon that describes the concentration gradient developed at a membrane/solution interface due to the permselectivity of a membrane [1]. This phenomenon increases the osmotic pressure gradient in the membrane, leading to fouling and salt leakage through the membrane [2]. Since fouling inevitably results in reduced separation efficiency, the life span of a membrane is reduced; therefore, detection of fouling in the early stage of development is highly desirable. Indeed, the monitoring of permeating flux and transmembrane pressure has been frequently reported to be not sensitive enough, particularly in the early stage of fouling development [3]. Recently, the technique of electrical impedance spectroscopy (EIS) has been introduced to measure changes in the electrical properties of a reverse osmosis (RO) system. Hu and co-workers noted that the change in conductance of an RO membrane occurs much earlier than any significant changes in permeate flux decline [4]. The accumulation of charged ions in both the skin layer and porous sublayer of a semipermeable membrane significantly increases the conductance during filtration [4]. A three-stage variation in the conductance, as well as in the flux, was identified; (i) in the first stage, concentration polarization occurs; (ii) in the second stage, nucleation occurs on the membrane surface; and (iii) in the last stage, the bulk precipitates once the critical concentration for the fouling formation is reached [5,6].

These reports clearly indicate that EIS can be used as a highly sensitive tool to detect the fouling process, particularly in the early stage. However, integrating EIS into a filtration system without compromising the high pressure resistance is challenging. In addition to the integrated system design, an interesting question appears regarding the interplay between changes in conductance and the capacitance recorded by EIS and existing models that were built based on observations of permeate flux and rejection. A potential answer might lie in the interactions between accumulated ions in permeating solution and the surface of membranes, known as the electroviscous effect. The electroviscous effect is a phenomenon in which an electric field near a charged surface (membrane) influences the distribution of a surrounding fluid (permeating solution) and consequently the viscosity of the fluid [7].

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In other words, an additional electrostatic force arising from the charged membrane surface can attract ions with opposite charge into the permeating solution, leading to an elevated viscosity at the membrane/electrolyte interface. This explains the observed pH-dependent permeating flux, which is particularly profound at low ionic strength or on highly charged surfaces [7]. On the other hand, accumulated ions on the membrane surface are expected to induce a localized high ionic strength regime at the solution/membrane interface, which would consequently compress the diffuse double layer around a charged particle and thus destabilize colloids [3]. Once destabilized colloids start to precipitate on membrane surfaces, a fouling layer develops that can subsequently compromise both the separation efficiency and the permeating flux.

Based on the discussions above, efforts were carried out in this study to establish the connections among conductance/capacitance, surface concentration polarization, permeating flux, and rejection. To this end, a new concept of pH equivalent (pHeq) was introduced, describing how the electrical property on a membrane surface will exhibit similar to that of a pH condition a membrane is conditioned. To establish a calibration curve for the pHeq, asymmetric polyamide thin-film membranes were first conditioned under different pH. The membrane conductance and capacitance (responsible for the electrical property on the membrane surface) in conditioned pH were then extracted *ex situ* using EIS. Filtration was then carried out with 0.1 mM Fe(III) chloride solution as a model reaction, and the conductance/capacitance of the membrane for different filtration times were recorded. Our results clearly indicated that variations in conductance and capacitance occurred long before any significant changes in the permeating flux and rejection. Significant changes in the conductance and capacitance together with compromised separation efficiency and permeating flux suggested that these phenomena are highly mutually dependent. The results are of significance for understanding the relationship between the chemistry and electrical properties of a membrane surface in a filtration system.

2. Materials and methods

2.1. Chemicals and procedures

All chemicals were of ACS grade, purchased from Sigma-Aldrich and Milli-Q water (18.2 MΩ) and used without any further purification. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) purchased from Merck KGaA (Darmstadt, Germany) were used to adjust the pH of feed solutions. The polyamide thin-film membrane (AD2540FM, GE Osmonics) was selected as a model membrane [8]. The membranes were conditioned by immersion in 100 mL 10 mM NaCl solutions (pH 2–pH 12) for 12 h before measuring their conductance and capacitance. The pH of the solution was monitored periodically and maintained at $\Delta pH < 0.05$ pH during conditioning. Then, the membranes were removed from solution and held vertically until liquid stopped dripping from the membrane. The membranes were then cut into slices (five samples for each condition) with sizes of 30 mm × 10 mm for the EIS measurement.

2.2. Filtration procedure

All filtration experiments were conducted using a homemade three-channel high pressure plate-and- frame membrane filtration system, with a dead-end configuration, as reported in our previous study [8]. The filtration cell was made by stainless steel, and the effective filtration area was 23.6 cm^2 (26.5 mm × 89 mm). Filtrations were conducted under pressure of 30 bars (435 psi) at a temperature of 28 ± 0.5 °C. The membranes were conditioned prior to filtration by immersion in 100 mL 10 mM NaCl solutions with pH 5, pH 7, and pH 9 for 12 h. Conditioned membranes were then mounted into the filtration system connected to a 5.0 L tank of feed water containing 0.1 mM Fe(III) chloride with identical pH. The filtration was allowed to run for a given period of time in triplicate, and the EIS spectrum of the membrane showing Fe(III) rejection closest to the average rejection value was presented. The permeating Fe(III) concentration (C_p) was measured using inductively coupled plasma optical emission spectrometry (ICP-OES 5100 DV, Agilent), with determination of the Fe(III) rejection (R) based on the following equation:

$$R = \left[1 - \frac{C_p}{C_0}\right] \times 100\%$$

where C_p and C_0 are the concentrations of Fe(III) in the permeate and feed solutions, respectively.

2.3. EIS collection and interpretation

The EIS in this study was recorded *ex situ* to minimize any potential influences arising from filtration cell assembly, although in situ EIS measurement has been successfully demonstrated in several studies using the cross flow tubular filtration cell [9,10]. To collect the EIS data, membranes were disassembled from the filtration cell following a set period of filtration time. To remove residual electrolytes, the samples were held vertically until liquid stopped dripping from the membrane. Assuming that the concentrated electrolytes in the concentration polarization layer were electrostatically attracted to the charged membrane and that the concentration polarization occurred homogeneously over the membrane surfaces, we speculate that the liquid dripping off the membrane possessed a chemical composition similar to that of the bulk solution (and therefore can be reasonably removed). This alternative drying process was expected to decrease interference from the bulk solution while maintaining a less affected status of the surface concentration layer. Similar to the membranes conditioned at different pH, membranes collected from the filtration experiments were cut into identical slices (30 mm × 10 mm, with five samples for each condition) prior to EIS measurement. EIS was carried out using a CHI electrochemical workstation (CHI 608E, CH Instrument) with stainless steel tweezers as electrical contacts (Fig. 1a, insert) at an applied bias of +0.1 V and frequency ranging from 100 kHz to 1 Hz. Note that the two-terminal ESI measurement is insufficient to accurately separate out impedance dispersion of the known component (*i.e.*, arising from the Gouy-Chapman double layer) from that of other unknown components [11]; therefore, the EIS was not measured in the low frequency regime (<1 Hz). Measured EIS spectra were then fitted to an equivalent circuit by trial and error using the Zview software (Scribner Associates Inc.). To minimize errors during the fitting process, the following protocols were followed based on several approximations and considerations. First, a 2-component model was adopted, as shown in Fig. 1b. Although the introduction of more variables can give a more precise fit to the measured data, the model enabled one to avoid introducing additional variables not supported by any physical basis. In this configuration, we assigned the first component to represent the membrane domain, while the second component represented the electrolyte-membrane interface. This assignment is based on two considerations; (i) both the active layer and the membrane support contain the electrolyte-membrane interface and the membrane domain; therefore, precise isolation of one from the other is challenging as sophisticated insulation in the contact is important for filtering environmental noise; (ii) the basic aim of EIS is to measure the response of an AC current passing through a circuit element (the membrane in this study) as a function of frequency. In this configuration, charge transport usually occurs in the high-frequency regime, with the motion of ions often observed in the low-frequency regime due to the much heavier ionic