임피던스 스펙트로스코피를 이용한 이온교환막 시스템에서의 **BSA** 막오염 특성분석

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**BSA fouling characterization of an ion-exchange membrane system using an electrical
impedance spectroscopy**

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Introduction

While ion-exchange membranes have been used mainly for production of deionized water from brackish water worldwide, emerging applications in environmental and biotechnology industry have been recently found [1, 2]. However, one of common problems in expanding applications for ion-exchange membranes is their fouling when handling solutions containing foulants. The foulants deteriorate membrane performances, indicated by a decline in the flux and an increase in the electric resistance [3, 4]. Bovine serum albumin (BSA) is one of the most common foulants in the electrodialysis process in the biotechnology industry. The macromolecular BSA is a protein which has an amphoteric property, and is too large to permeate through the ion-exchange membrane. It can be deposited on the surface of cation- and anion-exchange membranes depending on solution pH, resulting in irreversible fouling. Therefore, fouling characterizations should be carried out to evaluate electrochemical properties of newly prepared ion-exchange membranes or to monitor separation processes during the operation, aimed at minimizing the fouling. Although the intrinsic conductivity sometimes decreases abruptly when the membrane is fouled. The decrease can also be due to dilution of the ions in a diluate compartment, physical defect of the membranes, or chemical damage of membranes during operations.

In this study, the fouling characterization was evaluated by an electrical impedance spectroscopy method that is non-invasive and provides well-responded electrical properties for a targeted foulant in situ in order to get a better insight into the effects of the foulant on the fouling of ion-exchange membranes in terms of conductance and capacitance with frequency. Furthermore, it aims at providing an enhanced indication for membrane fouling in separation processes using ion-exchange membranes.

Materials and methods

Lyophilized bovine serum albumin powder (98% purity; Sigma, St. Louise, Missouri) and potassium chloride (Sigma, St. Louise, Missouri) in reagents grade was used as a foulant and a supporting electrolyte, respectively. Deionized water (18 MΩ-cm) was used in preparing all the electrolytes.

Neosepta CMX and AMX (Tokuyama Soda Co., Japan) are reinforced standard grade homogenous ion-exchange membranes containing fixed charges of sulfonic acid groups and quaternary ammonium groups, respectively. They are used for use in general concentration or desalination purposes.

Impedance spectroscopy was carried out on these membranes using a two-compartment electrodialytic cell with compartments of equal volume (150 mL) with the membrane supported in a circular hole between the compartments. The effective area of the membrane was 0.785 cm^2. The impedance of the membrane system was measured using two Ag/AgCl voltage electrodes immersed into Luggin capillaries and separate Ag/AgCl electrodes for injecting the current. The alternating current was supplied by the Biophysics Ultra Low Frequency Impedance Spectrometer (BULFIS) Marque II, developed in the department of Biophysics at the University of New South Wales. The four-terminal configuration minimized the contribution of the electrolyte-Ag/AgCl interfaces to measurements. A frequency scan from 104 kHz to 6.8 mHz was applied in all the experiments.

In order to investigate dispersions arising from BSA fouling effects on ion-exchange membranes, the AMX membranes were made fouled using 0.1 M KCl in the presence of 1% (w/w) BSA at 15 V constant direct current (d.c.) voltage because each half cycle of the alternating current at low frequencies was not long enough to lead the BSA fouling on anion-exchange membranes. Impedance spectra of the unfouled and fouled IEMS immersed in 0.1 M KCl were measured in the presence and absence of 1% (w/w) BSA.

Theory

The ratio of the voltage response ($v(\omega) = v_o e^{j(\omega t - \varphi)}$) of the system to an alternating current ($i(\omega) = i_o e^{j\omega t}$) of frequency ω defines the impedance, i.e.,

$$Z(\omega) = \frac{v(\omega)}{i(\omega)} = |Z|e^{-j\varphi} = |Z|\cos(\varphi) - j|Z|\sin(\varphi) = Z' - jZ'' \qquad [1]$$

where $|Z|(= v_o / i_o)$ is the impedance magnitude, $\omega(= 2\pi f)$ the angular frequency, and φ the phase difference between the voltage and current. The imaginary constant j is defined by j^2 = -1. Admittance is defined as the reciprocal of the impedance and is given by

$$Y(\omega) = \frac{1}{Z(\omega)} = \frac{i_o}{v_o}e^{j\varphi} = \frac{i_o}{v_o}\cos(\varphi) + j\frac{i_o}{v_o}\sin(\varphi) = G + j\omega C \qquad [2]$$

where G is the total conductance and C the total capacitance of the system. G and C provide information on charge conduction and storage properties, respectively.

An ion-exchange membrane system (IEMS) generally consists of a solution, a membrane, a diffusion boundary layer (DBL), and heterogeneous transport (such as ionic exchange between the solution and the membrane). The transport number for ions that are counter ions in the membrane is different from that for those ions in the two solutions. Usually, the transport number in the membrane is much higher than that in the bulk solution because the high concentration of the fixed charged groups of ion-exchange membranes enhances the concentration of counter ions. These circumstances give rise to formation of the DBL in which the total concentration of the electrolyte is elevated on one side of the membrane and depleted on the other side. The alternating field perturbs the DBL at very low frequencies. The field derives ions across the membrane in one direction whereas the concentration polarization effects of the DBL lead to oppose that flow. This induces a phase shift which can give rise to a pseudo-capacitance which is usually orders of magnitude larger than dielectric geometrical capacitances of the system [5]. Another origin of such phenomenological impedance arises from voltage electrodes perturbing the otherwise spatially constant current density resulting in a pseudo-phase shift of the voltage measured by those electrodes. In this respect, it is believed that the impedance measurements of an IEMS can be modeled with a lumped combination of several impedance elements. The elements derive from the bulk solution (including effects of the voltage electrodes) and the membrane (including effects of the DBL and heterogeneous transport). The impedance of the membrane is therefore given by

$$Z_m = Z_t - Z_s = \frac{1}{G_t + j\omega C_t} - \frac{1}{G_s + j\omega C_s} \qquad [3]$$

where the subscript "t" denotes measurements of total system (the membrane and solution) and the subscript "s" denotes measurement of the solution only. Alternatively the admittance of the membrane is given by

$$Y_m = \frac{1}{Z_m} = G_m(\omega) + j\omega C_m(\omega) = \frac{p \cdot q \cdot m}{m^2 + \omega^2 n^2} + j\omega \frac{p \cdot q \cdot n}{m^2 + \omega^2 n^2} \qquad [4]$$

where $p = G_t^2 + \omega^2 C_t^2$, $q = G_s^2 + \omega^2 C_s^2$, $m = G_t(G_s^2 + \omega^2 C_s^2) - G_s(G_t^2 + \omega^2 C_t^2)$, and $n = C_t(G_s^2 + \omega^2 C_s^2) - C_s(G_t^2 + \omega^2 C_t^2)$.

Results and discussion

Since BSA used in this study has a highly negative charge, it did not affect membrane fouling. Further results obtained from IEMSs using the AMX anion-exchange membrane will be discussed.

Fig. 1a shows that the addition of BSA to the unfouled and fouled IEMS produced decreases in the conductance at all frequencies. The decrease for the fouled IEM was the larger. Presumably the BSA in the solution adsorbed more readily to the BSA on the membrane surface. This made the fouling phenomena pronounced.

Moreover, it can be observed in Fig. 1a that the experimental variation in conductance (see error bars) of the fouled IEMSs in the BSA solution varied the most. A possible explanation is that a solution (free of BSA) interacts more favorably with the deposited BSA, arising from competitive interaction, between negatively charged BSA and chloride ions. The uppermost values of the conductance might correspond to the interaction of chloride ions and the lowermost values of the conductance the interaction of negatively charged BSA. Although the conductance change in Fig. 1a is sufficient to describe the fouling effect, the capacitance change in Fig. 1b does not provide an immediate indication of the effect.

Fig. 2 shows the impedance spectra for the membrane alone after subtracting contributions from the solution (plus electrode effects) using Eq. (4). The membranes fouled for 4, 18, and 22 hrs were examined. Fig. 2a shows a clear increase in the resistance by the BSA layer on the AMX membrane with increasing fouling time. This indicates that the BSA was accumulating on the membrane surface, resulting in an increase in thickness. Fig. 2a shows that the resistance exponentially increased with increasing fouling time. Assuming that the specific resistance of BSA deposited on the AMX membrane surface is constant with fouling time, this result is consistent with the postulation that the BSA in the solution is more likely to be deposited on the membrane surface.

The subtracted capacitance in Fig. 2b also shows a distinct decrease with increasing fouling time, indicating thickening of the BSA layer (note that the capacitance is inversely proportional to the thickness of the fouling layer).

The increase in resistance and decrease in capacitance confirmed that fouling occurred via the accumulation of the BSA on the AMX membrane.

Conclusion

An electrical impedance spectroscopy provided an enhanced indication for membrane fouling in separation processes using ion-exchange membranes. The subtraction technique described in this study eliminated the strong dispersion caused by the reference electrodes providing a clearer indication of the fouling from conductance and capacitance measurements.

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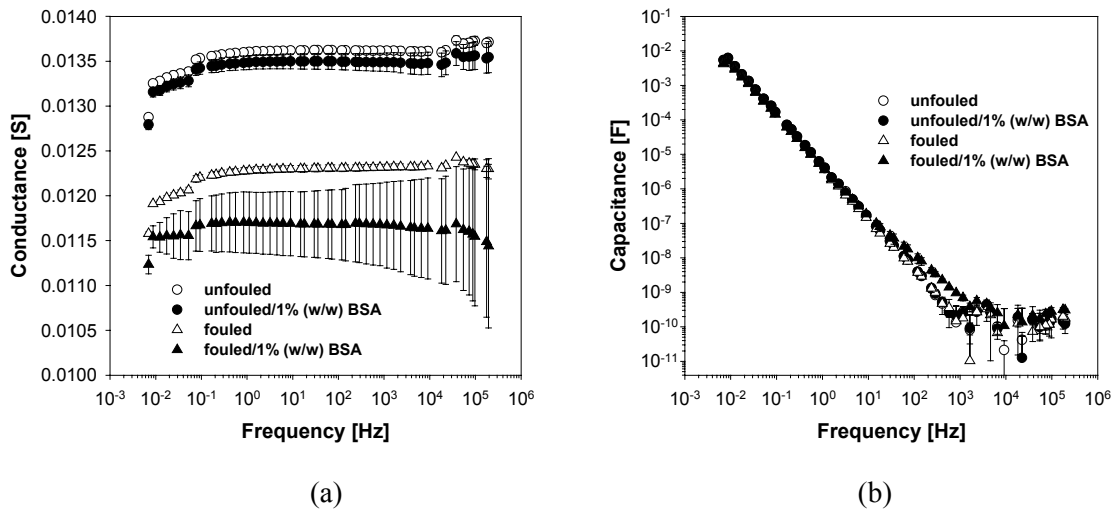(a)   (b)

Fig. 1. Dispersions of (a) the conductance (b) capacitance with frequency for the ion-exchange
membrane system in a 0.1 M KCl solution without and with 1% (w/w) BSA. The AMX membrane
used in these experiments was fouled by BSA at 15 V constant d.c. voltage for 18 hrs.

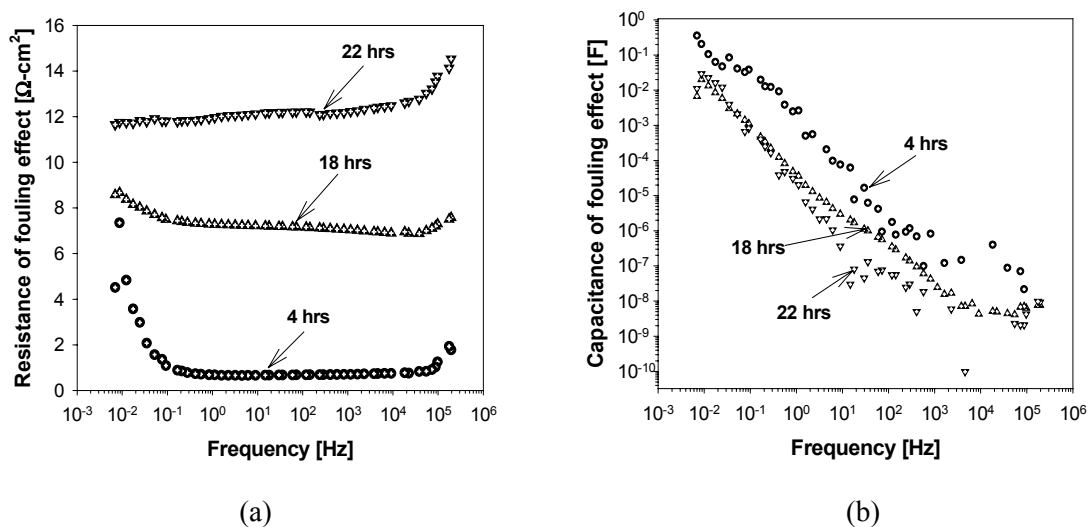(a)   (b)

Fig. 2. Subtracted (a) resistance and (b) capacitance with frequency using Eq. (5) with the admittance
data (see Fig. 1) for the ion-exchange membrane system using the fouled ion-exchange membrane at
15 constant d.c. voltage for each indicated operation time and that for the solution only.