

Capacitance Spectroscopy to Characterize Organic Fouling of Electrodialysis Membranes

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Published in *Journal of Membrane Science*, volume 162, page 213 (1999)

Abstract

Fouling of electrodialysis membranes by anionic organic substances is a widely recognized problem. We report a method to characterize fouling of anion-exchange membranes by dissolved anionic organic macromolecules (sulfonated lignin). The change of the frequency-dependent electrical capacitance of commercial ion exchange membranes is used to track the fouling process in real time. The measurements are performed in an aqueous solution containing both the organic foulant, and a representative mixture of inorganic materials. This simulates an application of electrodialysis to purge inorganics from the closed water cycle of a paper machine.

Keywords: Electrodialysis; Fouling; Water Treatment; Papermaking

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Introduction

Fouling of ion exchange membranes has been recognized as an important issue¹. Organic anions that foul anion exchange membranes are present in many streams of interest for the application of electro dialysis (grape must², groundwater³, milk whey⁴, paper machine water circuits⁵). The water that circulates in the paper machine system is termed 'white water'. We use a model inorganic white water composition representing average white water inorganic levels.

Some work on membrane fouling characterization has been reported^{6,7,8}. Introductions and in-depth discussions of electrical impedance methods can be found in the literature^{9,10}. Most membrane related publications deal with characterizing membranes and membrane properties^{11,12}.

The results from electrical impedance measurements are often complex and difficult to interpret. We have focused here on the capacitance of the electrical double layer between the solution and the anion exchange membrane. Capacitance spectroscopy (CS) has been used to characterize inorganic fouling¹³ and to characterize adsorption on other surfaces¹⁴. The term electrical double layer used here is as defined elsewhere¹⁵.

Our concept is that changes in the membrane/solution electrical double layer should be detectable as changes of the electrical capacitance of the system. Fouling of a membrane with macromolecules could then be identified and tracked by capacitance readings.

The capacitance as a tool to track fouling holds distinct advantages over measuring the DC resistance. Capacitance is rather insensitive to changes in the bulk solutions contacting the membrane. Addition of the organic foulant to the inorganic background solution or dilution of the background solution changed the DC resistance in our experiments by as much as 14% while the capacitance remained unchanged within the accuracy of the measurement. The capacitance has only a weak dependence on temperature and does therefore not require temperature correction within several degrees Celsius. This is very useful both in the laboratory, and for potential application of capacitance spectroscopy to monitor membrane performance in industrial applications.

Theory

Figure 1 shows a schematic of the system under investigation. No mass transfer (no DC electrical current) across the membrane is assumed to be present. The solution contacting the membrane is stagnant, and the system is equilibrated, isothermal, and symmetric. As displayed in Figure 2, this gives rise to four dielectric constants, κ , corresponding to the distinct phases between the electrodes (the two electrode/solution electrical double layers = κ_1 , the bulk solution on each side of the membrane = κ_2 , the two membrane/solution electrical double layers = κ_3 , and the membrane itself = κ_4). It is important to note that no net mass transfer is assumed to be ongoing, so that even when hydraulic boundary layers exist (hydraulic flow through the test cell), no non-equilibrium concentration gradients in the boundary layers are present that would convolute capacitance changes. No net mass transfer across the membrane is assumed because the

solutions on both sides of the membrane come from the same reservoir and there is no DC voltage gradient applied.

The capacitance developed between the two electrodes will depend upon the dielectric constant of each phase. The total capacitance C of the system can be calculated at any particular frequency as

$$C = \epsilon_0 A [\kappa_1\kappa_2\kappa_3\kappa_4/(\kappa_2\kappa_3\kappa_4d_1 + \kappa_1\kappa_3\kappa_4d_2 + \kappa_1\kappa_2\kappa_4d_3 + \kappa_1\kappa_2\kappa_3d_4)] \quad (1)$$

with ϵ_0 the permittivity of free space and A the cross sectional area of the electrodes. When an organic foulant is added and it adsorbs onto the membrane (Figure 1), the membrane/solution electrical double layer dielectric constant, κ_3 , will be changed¹⁶. Details on adsorption of our model foulant can be found elsewhere¹⁷. Changes in the membrane/solution electrical double layer such as the thickness, charge density, distribution of charges, and eventually the hindrance to mass transfer are the target of our frequency-dependent capacitance testing (Capacitance Spectroscopy, CS). In this paper we concentrate on the situation when net mass transfer is absent. A prerequisite to use this technique is that addition of the foulant does not significantly change the capacitance of the other five phases besides the two membrane/solution electrical double layers. This is shown below.

Experimental

The anionic organic foulant used was calcium lignosulfonate (65,000 weight average molecular weight). Nanopure water (18 M Ω -cm) was used to make all solutions.

The composition of the model inorganic background white water was 124 ppm Ca^{++} , 208 ppm Na^+ , 699 ppm SO_4^- , and 24 ppm Cl^- . Chemicals were of A.C.S. Reagent grade.

The test cell had a total volume of 200 ml, 100 ml on each side of the membrane (FuMaTech, St. Ingbert, Germany). The membranes were Tokuyama Corporation's Neosepta ACS anion exchange and CMS cation exchange membranes (Table 1). The total membrane area exposed to solution was 98 cm^2 (twice the active cross sectional membrane area of $3.5\text{cm} \times 14\text{cm}$). The membranes were conditioned by equilibrating them for 24 hours with seven successive batches of 0.3 liters of the model inorganic white water. The capacitance monitoring was performed with wire mesh titanium electrodes (see Figure 1). The anode was platinized

The capacitance measurements were performed using a computer controlled Quadtech 1689M LCR meter (Quadtech Inc., Marlborough, MA) that measured capacitances from 0.00001 pF to $99999 \text{ }\mu\text{F}$.

Experiments were performed by applying frequency sweeps to conditioned (see above) membranes that were either exposed to the inorganic background solution only, or to the background solution with added organic foulant. For equilibrium readings of fouled membranes, the membranes were equilibrated with the solution containing the foulant for 212 hours before frequency scans were performed. For each capacitance datapoint reported in Figure 3 below, three readings with the solutions or the solutions and membrane from three independent scans were averaged. The reproducibility was very good, so that the reproduced datapoints were virtually identical. The variation in the capacitance, except for the fouling case, was ± 0.2 percent. As discussed below, the

fouling is time dependent and the variation due to fouling is discussed separately. The time to complete one frequency sweep (from high to low frequency) is 20 minutes.

The foulant was introduced by removing the inorganic background solution from the test cell and then adding background solution containing the foulant. The frequency range was from 10 Hz to 100 kHz (sinusoidal, amplitude 0.01 Volt). The organic foulant (lignosulfonate) concentration change in solution from the initial 1000 ppm due to adsorption onto the membrane was below 1%. This was predicted from adsorption measurements of lignosulfonate on anion exchange resin beads. Equilibrium coverage of the membrane with the foulant can therefore be assumed when the adsorption process is complete.

Results

Figure 3 shows the capacitance as a function of frequency for the inorganic solution (no membrane, therefore only κ_1, κ_2), the inorganic solution containing the foulant (no membrane, κ_1^*, κ_2^*), the anion exchange membrane with inorganic solution ($\kappa_1, \kappa_2, \kappa_3, \kappa_4$), and for the anion exchange membrane with the inorganic solution containing the foulant ($\kappa_1^*, \kappa_2^*, \kappa_3^*, \kappa_4^*$). The capacitances are assigned to the different phases as shown in Figure 2. The superscript * denotes that the foulant has been introduced into the solution. The capacitance of the electrode/solution double layers or the bulk solution did not change measurably with the addition of the foulant to the bulk solution ($\kappa_1 = \kappa_1^*, \kappa_2 = \kappa_2^*$). Thus possible adsorption of the foulant onto the electrodes was not detectable by this method. Introduction of the membrane increased the capacitance especially in the high frequency range. This is expected because of the introduction of the membrane/solution electrical

double layer and the polarizable ion exchange groups of the membrane. Fouling the membrane again increased capacitance ($\kappa_3 \neq \kappa_3^*$), likely because charge was added to the membrane solution electrical double layer.

Thus, the capacitance increase in Figure 3 from the inorganic solution/membrane curve to the inorganic solution/foulant/membrane curve was due to fouling of the membrane. The capacitance increase was by as much as 24% whereas the variation in the capacitance for adding the not fouled membrane was only 0.2%. The capacitance not only increases overall when fouling occurs, but the change depends on the frequency. This shows the opportunity to not only detect fouling, but that the possibility might exist to identify the type of foulant from the subtle frequency dependency of the capacitance. Molecular compounds have been shown to have distinct dielectric constant versus frequency behavior¹⁸.

The change in κ_3^* was found to be a function of time. The 65,000 molecular weight foulant was likely too large for the molecules to enter the membrane and change the membrane dielectric constant due to information from the manufacturer concerning how tightly crosslinked the membranes are. The membrane dielectric constant could conceivably change significantly for a highly porous membrane, where a significant number of the interior ion exchange groups are accessible to a large foulant molecule. This is not the case here. We therefore can assume that the membrane phase is unaltered during fouling ($\kappa_4 = \kappa_4^*$). The dielectric constants κ_1 , κ_2 , κ_3 , and κ_4 did not vary from static values with the introduction of flow. The rate of change of κ_3^* was dependent on the flow conditions but maintained the same immediate value with cessation of flow.

In Figure 4 the capacitance change, at 4kHz, due to fouling of the anion exchange membrane is shown as a function of time (both with and without flow through the test cell). Time zero capacitance values are for the membrane in the inorganic only solution, which showed no time dependence. The average zero value for the anion exchange membrane was $(5.8 \pm 0.7) \times 10^{-9}$ F.

No fouling of cation exchange membranes was found. The capacitance of the system with a cation exchange membrane remained at $(1.69 \pm 0.02) \times 10^{-8}$ F, at 4 kHz, whether the foulant was present or not. The measurements were performed until 100 hours had elapsed. Two separate experiments on two different cation exchange membranes were performed.

Comparing the fouling rate for the predominantly 0.19 gallons per hour (gph) flow rate with the 8 gph flow rate indicates that the time to foul the membrane to the same capacitance value increased by a factor of approximately 2.5. Steady-state one-dimensional mass transport by diffusion through a stagnant hydraulic boundary layer would result in a linear dependence of the fouling rate on the hydraulic boundary layer thickness¹⁹. In a flow situation, the hydraulic boundary layer is the stagnant portion of the solution near the membrane surface. The steady-state one-dimensional conditions require the surface to act as a sink, giving a foulant concentration of zero near the surface. These conditions would prevail until significant surface coverage is achieved. Thus, with a constant bulk concentration of foulant, we arrive at a linear concentration gradient across the hydraulic boundary layer. Experimental results showed no foulant desorption thus supporting the sink assumption. The hydraulic boundary layer is typically several orders of magnitude thicker than the electrical double layer. For turbulent flow we

estimate that the lower flow rate (0.19 gph) would give a hydraulic boundary layer about 1.7 times thicker than the fast (8 gph) flow rate²⁰. For laminar flow the lower flow rate would give a hydraulic boundary layer 6.5 times thicker. The dependence of the experimentally observed fouling rate on the flow rate is in the expected range for diffusion limited mass transport of the foulant across a hydraulic boundary layer¹⁷. However, this conclusion requires that the adsorption versus time response be linear, which it is not. Thus, some other factor, such as surface availability restrictions, may also be constraining the adsorption rate. Insufficient data is available at this time to determine the limitation to the adsorption rate. From the comparison of the time dependence of the capacitance readings with the timescale of diffusion limited adsorption one can therefore conclude that the capacitance readings monitor the actual foulant adsorption process.

Concluding Remarks

Capacitance measurements of anion exchange membranes give information on the fouling of the membranes by organic macromolecules, both in no-flow and under flow conditions. The fouling can be tracked in real time. The membrane/solution electrical double layer governs the results of capacitance measurements.

Further work with other organic foulant molecules is under way. The goal is to conclude from capacitance measurements to the behavior and type of membrane fouling. Also, a detailed physical model of the adsorption process at the membrane surface is being developed.

Acknowledgements

Financial support by the US Department of Energy, contract W-31-109-Eng-38, is gratefully acknowledged. Portions of this work were used by E. J. W. as partial fulfillment of the requirements for the Ph.D. degree at the Institute of Paper Science and Technology.

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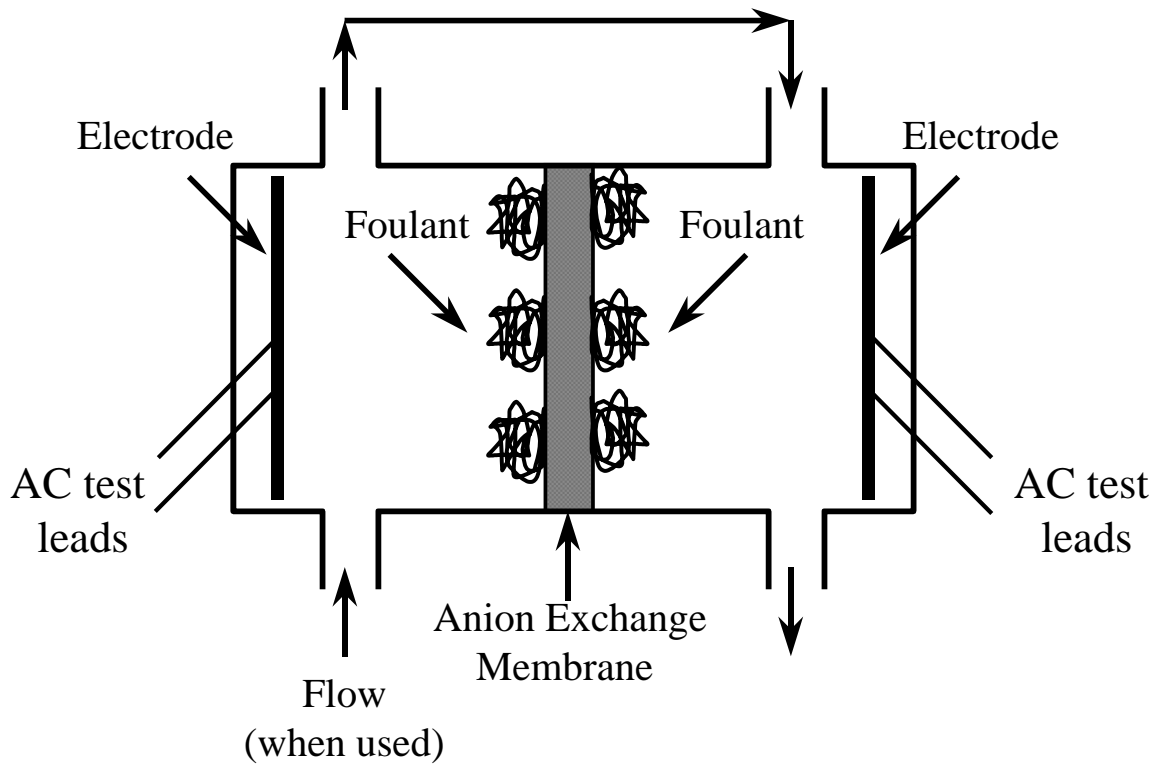


Figure 1 Capacitance spectroscopy symmetric test cell with membrane in place.

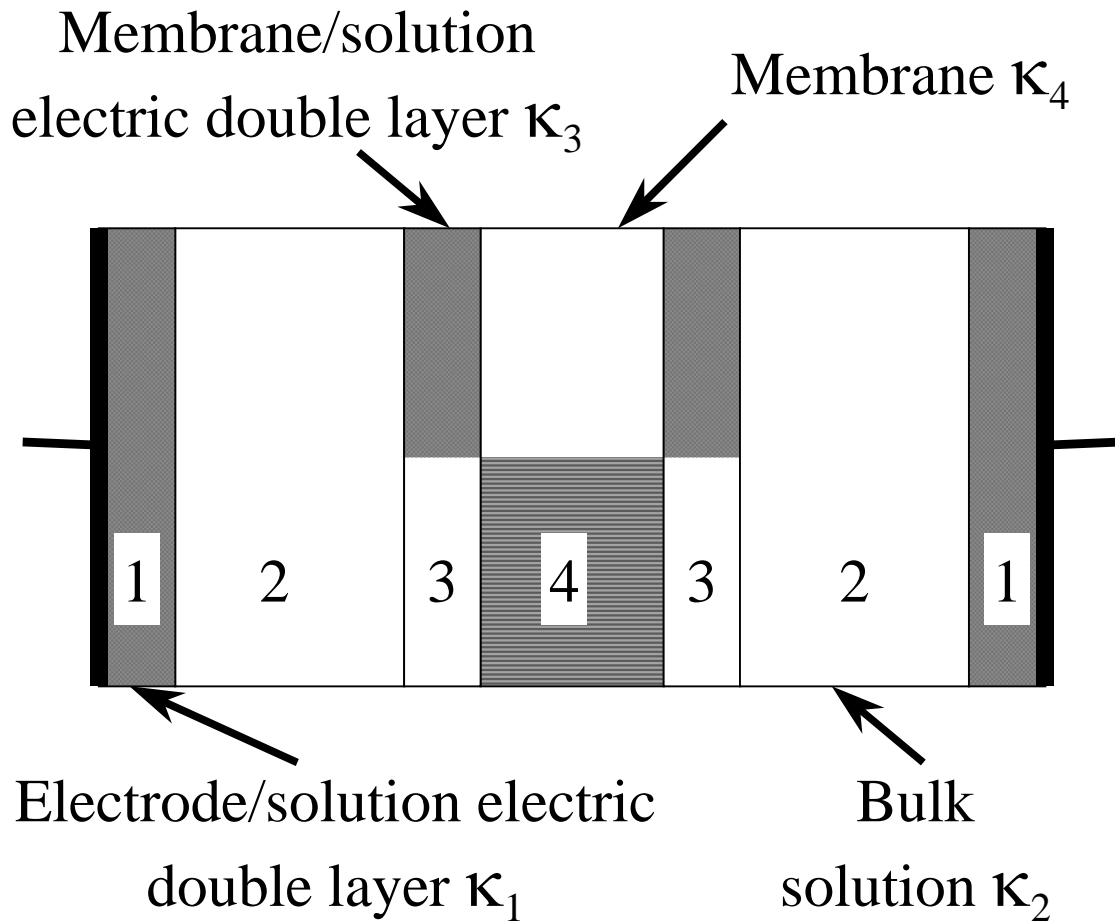


Figure 2 The seven distinct test cell phases and the four associated dielectric constants.

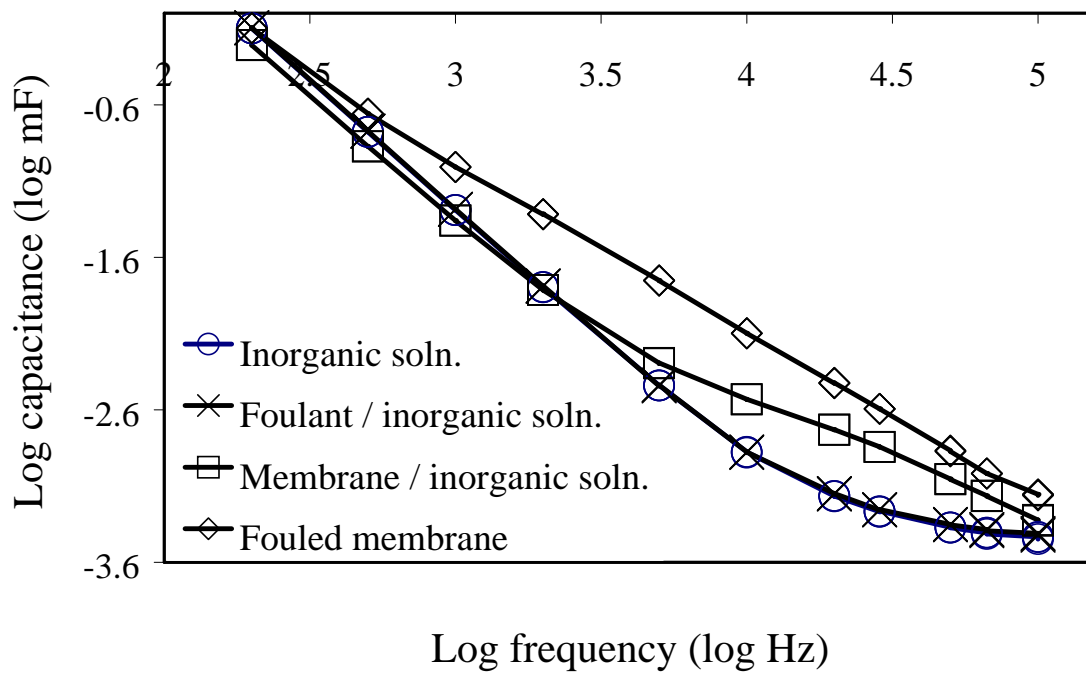


Figure 3 Capacitance versus frequency for the inorganic background solution, and with an anion exchange membrane, and foulant added.

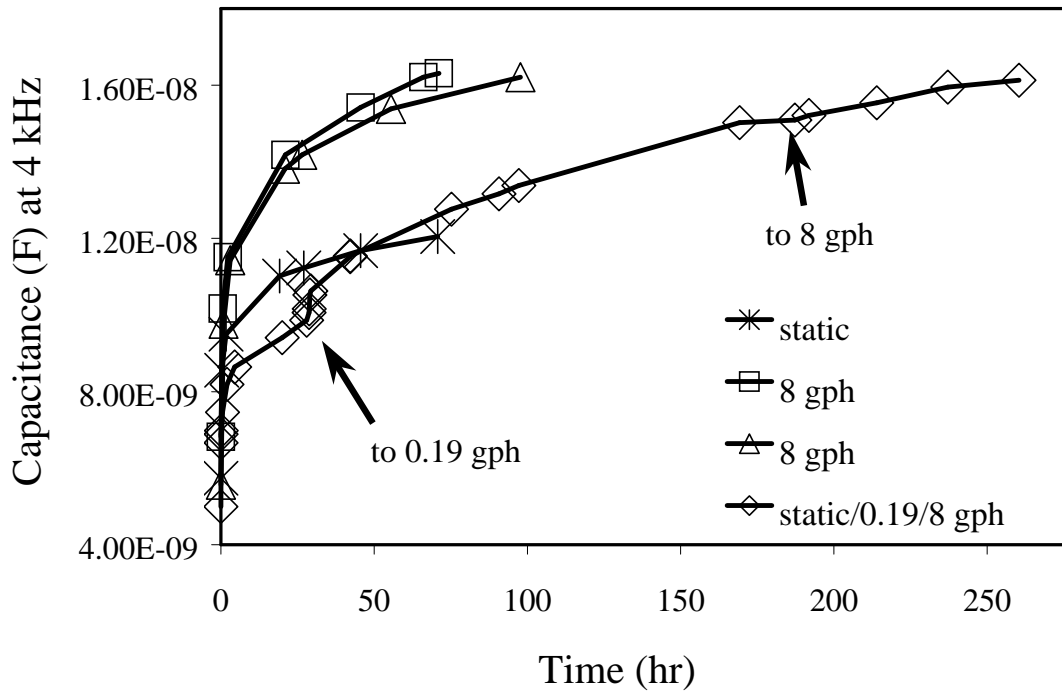


Figure 4 Fouling of anion exchange membranes expressed as capacitance at 4 kHz vs. time (gph: gallons per hour).

	Cation exchange membrane	Anion exchange membrane
tradename	Neosepta [®] CMS	Neosepta [®] ACS
type	strongly acidic monovalent selective	strongly basic monovalent selective
resistance [Ωcm^2]	1.5 - 2.5	2.0 - 2.5
thickness [mm]	0.14 - 0.17	0.15 - 0.20
exchange capacity [mequiv.g ⁻¹ dry resin]	2.0 - 2.5	1.4 - 2.0

Table 1

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