An Electrochemical Immittance Analysis of the Dielectric Properties of Self-Assembled Monolayers

<table>
<thead>
<tr>
<th>Journal:</th>
<th>Canadian Journal of Chemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manuscript ID</td>
<td>cjc-2020-0005.R1</td>
</tr>
<tr>
<td>Manuscript Type:</td>
<td>Article</td>
</tr>
<tr>
<td>Date Submitted by the Author:</td>
<td>27-Feb-2020</td>
</tr>
<tr>
<td>Complete List of Authors:</td>
<td>Dionne, Eric; Université de Montréal, Chimie Ben Amara, Fadwa; Université de Montréal, Chimie Badia, Antonella; Université de Montréal, Chimie</td>
</tr>
<tr>
<td>Is the invited manuscript for consideration in a Special Issue?:</td>
<td>University of Montreal</td>
</tr>
<tr>
<td>Keyword:</td>
<td>self-assembled monolayer, dielectric properties, ionic insulator, electrochemical impedance spectroscopy</td>
</tr>
</tbody>
</table>

Note: The following files were submitted by the author for peer review, but cannot be converted to PDF. You must view these files (e.g. movies) online.

cjc-2020-0005r2_figures.docx
An Electrochemical Immittance Analysis of the
Dielectric Properties of Self-Assembled Monolayers

Eric R. Dionne, Fadwa Ben Amara, and Antonella Badia

Département de chimie, Université de Montréal, C.P. 6128, succursale Centre-ville,
Montréal, QC H3C 3J7 CANADA

Corresponding author: Antonella Badia (antonella.badia@umontreal.ca)
Abstract

The ability of organic self-assembled monolayers (SAMs) to act as insulating barriers to charge and ion transport or molecular diffusion is critical to their application in a variety of technologies. The use of appropriate analytical tools to characterize the dielectric properties of these molecular thin films is important for the control of structural defects and establishing structure–property relations. In this context, we analyze the ionic permeability and dielectric response of SAMs formed from a homologous series of \( n \)-alkanethiylates (\( \text{CH}_3(\text{CH}_2)_n\text{S} \), where \( n = 9, 11, 13, 15, 17, \) and 19) on gold using the immittance quantities of the complex impedance, capacitance, and permittivity available from the same electrochemical impedance spectroscopy (EIS) measurement. The most sensitive parameters and frequency range for characterizing the capacitive behavior and assessing the ion-blocking quality of the SAMs under non-faradaic conditions are identified. We also investigate the effect of chain length on the interfacial capacitance and dielectric constant of ionic insulating SAMs. The advantages of the capacitance quantity and related permittivity data over traditional impedance representations and equivalent electric circuit modeling are discussed.
Key words: self-assembled monolayer, dielectric properties, ionic insulator, electrochemical impedance spectroscopy
Introduction

Organothiols chemisorb to noble metal surfaces, forming well-defined two-dimensional (2D) films coined "self-assembled monolayers" (SAMs).\textsuperscript{1-4} These monomolecular layers are integral components of nanotechnology,\textsuperscript{2} in organic/molecular electronics (capacitors, gate dielectrics for low-voltage FETs, junctions),\textsuperscript{5} soft lithography,\textsuperscript{6} and surface-based biomolecular sensors\textsuperscript{7,8}. The density of structural defects and pinholes in the SAM (i.e., sites for molecular and ion penetration or electron transport to the underlying metal surface) must be low for this nanometer thick film to act as an effective barrier to chemical etchants, non-specific adsorption, charge accumulation or charge transfer. Electrochemical methods to characterize the structural integrity and insulating character of SAMs include cyclic voltammetry (i.e., oxidoreduction of soluble redox species, gold oxide formation/stripping, and underpotential deposition/stripping of metals) and electrochemical impedance spectroscopy (EIS).\textsuperscript{9} The latter ac technique measures the resistive and capacitive properties of electrochemical cells.\textsuperscript{10} It can be used to characterize ionic or electronic conductors as well as dielectric materials.\textsuperscript{11} The frequency-resolved aspect of EIS is especially powerful as it probes conduction (electrical
and ionic) and electron transfer processes occurring at material/electrolyte interfaces over time scales of microseconds (MHz) to seconds (Hz to subHz).\textsuperscript{12} Non-faradaic EIS has been used to investigate the permeability of SAMs to electrolyte ions, their electrochemical stability, the effect of substrate roughness, and potential-induced change in the SAM microstructure.\textsuperscript{13-25}

A library of mathematically-related immittance functions is available from a single EIS measurement (i.e., complex impedance, admittance, capacitance, permittivity, and dielectric modulus).\textsuperscript{10, 12, 26} Analyses of film-modified electrodes generally consider only the raw complex impedance data.\textsuperscript{13-22, 24} However, an immittance approach more fully captures the dielectric signature and ionic conductivity of the SAM. Specifically, the complex impedance representation emphasizes values at low frequency and is often used to identify Faradaic processes parallel to the double-layer capacitance.\textsuperscript{10} By contrast, complex admittance and capacitance representations emphasize values at high frequency and are better suited to the analysis of blocking electrodes, for which information is ultimately sought on the system capacitance, or parallel processes whose time constants differ due to different resistive components.\textsuperscript{10, 11} For example, Góes et al.
demonstrated the unique capability of capacitance spectra to separate field-induced ion migration within the film at low frequency from the ionic dipolar relaxation of the SAM at higher frequency for Au/SAM/electrolyte interfaces behaving as leaky capacitors.\textsuperscript{23} Additionally, in a study of potential-induced defects in SAMs, Boubour and Lennox observed a sharp increase in the absolute magnitude of the permittivity at low frequency due to the penetration and accumulation of ions and solvent into the low dielectric hydrocarbon region of the SAM.\textsuperscript{16} These investigations clearly demonstrate the greater sensitivity of the impedance-derived capacitance and permittivity quantities over the measured impedance at exposing the ionic permeability of low conductivity structures like SAMs.

The present work uses the complex impedance, capacitance, and permittivity functions to analyze the dielectric behavior of SAMs of $n$-alkanethiolates ($\text{CH}_3(\text{CH}_2)_n\text{S}$) on gold at a structurally non-perturbing applied dc potential and in the absence of a redox probe. The focus is on the capacitance and relative permittivity as these properties are used as figures of merit to characterize the performance of organic dielectric layers.\textsuperscript{27, 28} We first consider the responses of $\text{CH}_3(\text{CH}_2)_{11}\text{SAu}$ SAMs with varying degrees of ionic
permeability or leakiness to establish the most sensitive parameters and relevant frequency range for characterizing the capacitive behavior and evaluating the ion-blocking quality of the SAM. We then investigate the effect of chain length on the interfacial capacitance and dielectric constant of ionic insulating SAMs. *This work differs from previous investigations employing EIS to characterize the dielectric characteristics of CH$_3$(CH$_2$)$_n$SAu SAMs in the broader frequency range probed (0.1 Hz–1 MHz) to assess the SAM permeability*,$^{13-17, 19, 20, 22, 24, 25}$ *and the use of ion-blocking SAMs with near-ideal capacitor behavior for the study of the chain length dependence*.$^{23}$

**BACKGROUND**

**Relationship between Impedance, Capacitance, and Relative Permittivity**

EIS applies a low-amplitude, sinusoidal ac potential (typically 5–10 mV peak-to-peak) of a given frequency with a dc-offset potential to the electrochemical cell.$^{10, 26}$ The response to this potential perturbation is an ac current signal. The impedance $\hat{Z}$ can be expressed mathematically as the complex (frequency-dependent) ratio of the input


potential and measured current output. \(^{10, 29, 30}\) \(\hat{Z}\) is generally represented as a complex number:

\[
\hat{Z}(\omega) = Z'(\omega) + jZ''(\omega)
\]  

(1)

where \(Z\) and \(Z''\) are the real and imaginary parts, \(j\) is the imaginary unit \((-1)^{1/2}\), and \(\omega\) is the angular frequency of the potential (i.e., \(\omega = 2\pi f\) where \(f\) is the applied frequency in Hz). \(Z\) is the resistance of the system to current flow and \(Z''\), the reactance, describes the opposition to changes in the current flow. The absolute impedance magnitude \(|\hat{Z}|\) is given by:

\[
|\hat{Z}(\omega)| = \sqrt{Z'(\omega)^2 + Z''(\omega)^2}
\]  

(2)

Mathematical equations for \(Z'(\omega)\) and \(Z''(\omega)\) of the equivalent electric circuits commonly used to fit the impedance response of SAM-modified electrodes are given in Table 1.

Analogous expressions for the complex capacitance \(\hat{C}(\omega)\) and complex relative permittivity \(\hat{\epsilon}(\omega)\), also commonly referred to as the complex dielectric constant, are given

---

**Table 1**

<table>
<thead>
<tr>
<th>Equivalent Electric Circuit</th>
<th>Mathematical Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacitance</td>
<td>(\hat{C}(\omega))</td>
</tr>
<tr>
<td>Resistance</td>
<td>(Z'(\omega))</td>
</tr>
<tr>
<td>Reactance</td>
<td>(Z''(\omega))</td>
</tr>
<tr>
<td>Dielectric Constant</td>
<td>(\hat{\epsilon}(\omega))</td>
</tr>
</tbody>
</table>
in Table 2. \( C \) corresponds to the effective double-layer capacitance and \( \epsilon' \) is the relative permittivity. At low frequency, \( \epsilon' \) and \( C \) adopt static values. The imaginary components \( C'' \) and \( \epsilon'' \) are associated with losses in the form of energy dissipation. \( \mathcal{Z}(\omega) \) is related phasorially to \( \hat{C}(\omega) \):\(^{10, 23, 31}\)

\[
\hat{C}(\omega) = \frac{1}{\mathcal{Z}(\omega)(j\omega)} \quad (3)
\]

The real part \( C \) is related the imaginary part \( Z'' \) and the imaginary part \( C'' \) is related to the real part \( Z \). Assuming a Helmholtz parallel plate capacitor model for the gold/SAM/electrolyte interface, \( \hat{C}(\omega) \) can be reported in terms of \( \hat{\epsilon}(\omega) \):

\[
\hat{C}(\omega) = -\frac{\hat{\epsilon}(\omega)\epsilon_o A}{d} \quad (4)
\]

where \( \epsilon_o \) is the permittivity of free space (8.85419 \times 10^{-12} \text{ F m}^{-1}), A is the electrode area, and \( d \) is the SAM film thickness.\(^{23, 29, 30}\) The primary impedance data, \( Z'(\omega) \) and \( Z''(\omega) \), can thus be used to generate capacitance and relative permittivity spectra (Table 2), which highlight the electrical energy storage and dissipative characteristics of the system rather than its resistive properties (impedance).
The other impedance-related quantities are the complex admittance ($\dot{Y}$) and dielectric modulus ($\hat{\mathcal{M}}$). These quantities are merely the reciprocals of $\dot{Z}$ and $\dot{\varepsilon}$, respectively, and are not considered here.

**Equivalent Electric Circuit Representations of the SAM-Modified Metal Interface**

The equivalent circuits employed to fit the non-faradaic impedance response of SAM-modified metal electrodes at a structurally non-perturbing dc potential and examples of impedimetric complex plane plots ($Z'$ vs $Z'$) are shown in Fig. 1. The Helmholtz-type equivalent circuit I, consisting of a solution resistance $R_s$ in series with a constant phase element (CPE), describes defect-free ion-blocking SAMs.\textsuperscript{13, 15, 20, 32} SAMs presenting defect sites for ion permeation are modeled using the Randles-type circuit II, which includes a resistance $R_{\text{SAM}}$ in parallel with the CPE.\textsuperscript{18, 21, 22, 33} When $R_{\text{SAM}} > \sim 10^8 \ \Omega \ \text{cm}^2$, the impedance response of the SAM can be fit using circuit I.

The use of a CPE in the place of a capacitor to model the interfacial capacitance $C$ significantly improves the quality of the fits of the experimental data. The CPE is a power law-dependent parameter that accounts for deviations from pure capacitor behavior. The impedance of a CPE $\hat{Z}_{\text{CPE}}(\omega)$ is given by the relation:

\[ \hat{Z}_{\text{CPE}}(\omega) = \frac{1}{\dot{Z} \omega^{\alpha}} \]

https://mc06.manuscriptcentral.com/cjc-pubs
\[
\hat{Z}_{\text{CPE}}(\omega) = \frac{1}{T(j\omega)^\alpha}
\]

where \( T \) is the parameter related to the electrode capacitance and \( \alpha \) is the constant phase exponent \((0 < \alpha \leq 1)\). When \( \alpha = 1 \), the impedance of the CPE is equivalent to that of an ideal capacitor. In practice, a deviation from unity (e.g., \( 0.9 < \alpha < 1 \)) is almost always observed, even for a near-perfect blocking film, due to the nanoscale surface roughness and polycrystallinity of the underlying solid electrode causing local variations of the current density in the double layer.\(^{15,19}\) When \( \alpha \approx 0.99 \), \( C \) is assigned the value of \( T \) and the difference in the units of \( T \) (F s\(^{1-\alpha}\) cm\(^{-2}\)) and \( C \) (F cm\(^{-2}\)) is ignored.\(^{34}\)

The total electrochemical capacitance of the SAM-modified electrode is approximated by two capacitors in series:

\[
C^1 = C_{\text{SAM}}^{-1} + C_D^{-1}
\]

where \( C_{\text{SAM}} \) is the capacitance of the SAM and \( C_D \) is the concentration-dependent diffuse layer capacitance of the electrolyte solution.\(^{9,13,21,23,24}\) For densely-packed SAMs, \( C_D \) is
at least an order of magnitude larger than $C_{\text{SAM}}$ so that its contribution to the total capacitance and $T$ can be neglected, as demonstrated experimentally by prior studies.\textsuperscript{13}

Experimental

Materials

The following \(n\)-alkanethiols and reagents were purchased and used without further purification: 1-decanethiol (CH\(_3\)(CH\(_2\))\(_9\)SH, 96%, Sigma-Aldrich), 1-dodecanethiol (CH\(_3\)(CH\(_2\))\(_{11}\)SH, \(\geq 97\%\), Fluka), 1-tetradecanethiol (CH\(_3\)(CH\(_2\))\(_{13}\)SH, \(\geq 98\%\), Fluka), 1-octadecanethiol (CH\(_3\)(CH\(_2\))\(_{17}\)SH, 98% Sigma-Aldrich), and sodium perchlorate (\(\geq 98\%\), Sigma-Aldrich). 1-Hexadecanethiol (CH\(_3\)(CH\(_2\))\(_{15}\)SH, > 95%, Sigma-Aldrich) was purified by column chromatography prior to use (SiO\(_2\), hexane:pentane (1:1 v/v), \(R_f = 0.75\)). 1-Eicosanethiol (CH\(_3\)(CH\(_2\))\(_{19}\)SH) was synthesized from CH\(_3\)(CH\(_2\))\(_{19}\)OH (98%, Sigma-Aldrich) by refluxing with 48% HBr to produce CH\(_3\)(CH\(_2\))\(_{19}\)Br followed by reaction with thiourea.\textsuperscript{35} Ultrapure water with a resistivity of 18.2 M\(\Omega\) cm and total organic carbon of \(\leq 5\) ppb (MilliQ Gradient) was used to prepare the electrolyte solution, rinse all surfaces, and as the probe liquid in the contact angle measurements.

Preparation of CH\(_3\)(CH\(_2\))\(_n\)S\textsubscript{Au} SAMs for Electrochemical Impedance Spectroscopy
Gold bead electrodes (99.99%) of surface area of 0.20 to 0.28 cm$^2$ were used for the electrochemical measurements. The electrodes were first sonicated in a 2:1 (v/v) mixture of 30% NH$_4$OH/30% H$_2$O$_2$ for 60 min, rinsed copiously with ultrapure water, and subjected to a 15 min treatment in an oxygen-plasma cleaner at medium RF power setting (Harrick model PDC-32G). Prior to SAM formation, the gold bead was immersed in dilute aqua regia (3:1:6 HCl/HNO$_3$/H$_2$O) for ca. 10 min to dissolve away gold and impurities from the bead surface, rinsed copiously with ultrapure water, and sonicated in ultrapure water for 2 min to remove traces of acid. Finally, the bead was flame-annealed and quenched in ultrapure water thrice and rinsed thoroughly with absolute ethanol.

The bead was immersed in an ethanolic solution of 0.2 mM CH$_3$(CH$_2$)$_n$SH for 18–24 h at room temperature in a sealed incubation vial. Prior to use, the SAM-modified bead electrode was removed from the CH$_3$(CH$_2$)$_n$SH solution, rinsed copiously with absolute ethanol followed by ultrapure water, and dried with nitrogen.

**Preparation of CH$_3$(CH$_2$)$_n$SAu SAMs for Contact Angle Measurements**

Premium quality glass slides cut into pieces of 20 mm × 25 mm were first cleaned by immersion in a solution of 3:1 v/v concentrated H$_2$SO$_4$/30% H$_2$O$_2$ (Warning - piranha solution is a strong oxidizer. Handle with extreme caution!) at room temperature. The glass slides were rinsed copiously with ultrapure water, sonicated thrice in ultrapure water to completely remove traces of sulfuric acid, sonicated once in absolute ethanol, and dried under a stream of nitrogen gas.
The clean glass slides were coated with titanium and gold by thermal evaporation (VE-90 vacuum evaporator, Thermionics Vacuum Products). The deposition of metal was initiated at a pressure of \( \sim 3 \times 10^{-7} \) Torr. An adhesion layer of titanium (99.99%) of 5 nm thickness was first deposited onto the glass at a constant rate of 0.01 nm s\(^{-1}\). The substrates were heated to \( \sim 200 \) °C with a UV lamp before the start of the gold evaporation. A 150 nm layer of gold (99.99%) was deposited while gradually varying the rate from 0.1 nm s\(^{-1}\) for the deposition of the first 65 nm to 0.01 nm s\(^{-1}\) for the final 40 nm. The substrate temperature was maintained between 200 °C and 240 °C during the gold deposition process by regulating the intensity of the UV lamp.

After cooling down to room temperature, the gold-coated glass slides were removed from the evaporator chamber and immediately immersed in ethanolic solutions of 0.2 mM CH\(_3\)(CH\(_2\))\(_n\)SH. The gold substrates were incubated for 16–24 h at room temperature in sealed incubation vials. Prior to a measurement, the SAM-functionalized gold-coated slide was removed from the incubation solution, thoroughly rinsed with pure ethanol followed by ultrapure water, and dried under nitrogen.

**Electrochemical Impedance Spectroscopy (EIS)**

EIS measurements on the CH\(_3\)(CH\(_2\))\(_n\)SAu SAMs formed on gold bead electrodes were carried out using a three-electrode glass cell thermostatted with a circulation water bath and SP-200 potentiostat (BioLogic Science Instruments) equipped with an impedance analyzer. The electrolyte solution, 1.0 M NaClO\(_4\)\(_{aq}\), was deoxygenated by bubbling nitrogen into the electrochemical cell for 20 min before the start of an experiment. Measurements were carried out under a blanket of nitrogen at 22.0 ± 0.1 °C. Impedance spectra were acquired over a frequency span of 7 decades, from 1 MHz to 0.1 Hz, at 32 points per decade using an ac voltage amplitude of 10 mV and an
applied voltage of -0.185 V versus Ag/AgCl, which is positive of the potential of zero charge measured for CH$_3$(CH$_2$)$_n$SAu SAMs in 0.1 M HClO$_4$(aq) (-0.53 V to -0.51 V for $n = 9$–17)$^{37}$. SAMs behave as ionic insulators at this dc potential.$^{14}$ ZView software (version 3.4f, Scribner Associates) was employed for complex nonlinear least-squares (CNLS) fitting of the impedance data to an appropriate electrical equivalent circuit.

Contact Angle Measurements

Static contact angle measurements were carried out using a homemade setup consisting of a micrometer syringe (Oakton Gilmont) to manually dispense a 2.0 μL droplet of probe liquid onto the SAM surface and a USB digital microscope to capture images of the liquid droplets on the surface. 8–10 droplets of ultrapure water were deposited on each SAM-modified gold-coated slide. Images of the droplets were analyzed using the contact angle plugin of Image J (NIH) to determine the contact angle formed between the SAMs and water droplets.

Results and Discussion

**Immittance Spectra of Ionic Insulating versus Leaky SAMs**

We begin by comparing the impedance responses of three CH$_3$(CH$_2$)$_{11}$SAu SAMs whose degree of ionic permeability or leakiness follows the order SAM 3 > SAM 2 > SAM 1 (Table 3). The impedimetric complex plane plot (Fig. 2a) of the insulating (ion-blocking)
SAM 1 is a nearly vertical line parallel to the y-axis that can be described by the equivalent circuit I, $R_e + \text{CPE}$, over the entire frequency range of 1 MHz to 0.1 Hz. We also fitted the impedance data of this SAM using the circuit II, $R_e + \text{CPE}||R_{\text{SAM}}$, to show that its resistance to ion permeation is a factor of 10–100 higher than that of the leaky SAMs 2 and 3 (Table 3). By contrast, the $Z''-Z'$ plots of the leaky SAMs 2 and 3 deviate from the vertical line and exhibit pronounced curvature at frequencies $< \sim 10$ Hz. These SAMs behave as a capacitor contaminated by a resistive component related to current leakage at defect sites and must be fit using the equivalent circuit II.

Bode plots of the impedance magnitude $|Z|$ of the three SAMs show no significant differences (Fig. 2b). $|Z|$ at 0.1 Hz is high at 2–3 MΩ cm$^2$. The slopes of the region of linear dependence of $|Z|$ on the logarithm of frequency (0.1 Hz–10 kHz) are -0.991, -0.989, and -0.997 for SAMs 1, 2, and 3, respectively. The slope corresponding to purely capacitive behavior is -1. The measured impedance is dominated by the solution resistance $R_e$ at high frequencies so that $|Z|$ becomes independent of frequency. A look at the frequency dependence of the individual $Z'$ and $Z''$ components (Fig. 2c) reveals that the magnitudes of $Z''$ at 0.1 Hz are comparable for SAMs 1 and 2, while that of the leakier SAM 3 is lower.
The $Z'$ values at 0.1 Hz of the leakier SAMs 2 and 3 are significantly larger than that of the ion-blocking SAM 1. The magnitude of $Z'$ follows the fitted value of $R_{\text{SAM}}$, where a higher $R_{\text{SAM}}$ corresponds to a lower $Z': R_{\text{SAM}} = 380 \, \text{M}\Omega \, \text{cm}^2$ (1), 13 $\text{M}\Omega \, \text{cm}^2$ (2), and 3.9 $\text{M}\Omega \, \text{cm}^2$ (3). This difference between the leaky SAMs 2 and 3 and insulating SAM 1 is lost in the Bode plots of $|Z|$ because the magnitude of $Z''$ is much larger than that of $Z'$, and in the case of the leakier SAM 3, a higher $Z'$ compensates the lower $Z''$.

Most significantly, the insulating SAM 1 presents a phase angle $\varphi$ of 89° between 1.0 and 0.1 Hz (Fig. 2d). An ideal capacitor exhibits $\varphi$ of 90° at all frequencies. Current leakage through the dielectric layer of the capacitor results in a deviation from 90°. The phase angles of the leaky SAMs exhibit such a deviation; $\varphi$ for SAM 2 decreases from 88° at 1.0 Hz to 83° at 0.1 Hz while $\varphi$ for SAM 3 varies from 87° at 1.0 Hz to 73° at 0.1 Hz. The phase angle approaches zero at higher frequencies when $R_e$ dominates the total impedance. Boubour and Lennox previously considered SAMs exhibiting a phase angle $\geq 88°$ at 1–10 Hz to be effectively free of defects. The minimum frequency they probed was 1 Hz. We however find that a more stringent discrimination between insulating and leaky SAMs requires probing lower frequencies, i.e., between 1 and 0.1 Hz. These
frequencies are more in line with the rate of ionic conduction (permeation) processes in SAMs 2 and 3, given by the product \((R_{\text{SAM}} \times \tau)^{-1}\), which falls between 0.01 and 0.1 Hz. For example, although \(\phi\) of SAM 2 is 88° at 1–10 Hz, it behaves as a leaky capacitor at lower frequencies, and a Helmholtz-type model cannot be used to describe its impedance response (Fig. 2a). Our analysis of more than 130 CH\(_3\)(CH\(_2\))\(_n\)S-modified gold electrodes establishes that a \(\phi\) of \(\geq 89°\) at 1 Hz is generally required for the Au/SAM/electrolyte interface to behave as a near ideal capacitor down to 0.1 Hz.\(^{15}\)

We now turn to the real \(C\) and imaginary \(C'\) components derived from \(Z'\) and \(Z\), respectively (Table 2), to reveal differences in the capacitive behavior of the three CH\(_3\)(CH\(_2\))\(_{11}\)SAu SAMs. The capacitive complex plane plots (Fig. 3a) show semicircles of similar diameters for SAMs 1 and 2, and hence directly report that these SAMs have nearly identical capacitances, while SAM 3 has a larger (diameter) capacitance. The \(C'\) values at 0.1 Hz (Fig. 3b) yield static capacitances of 1.08 \(\mu\)F cm\(^{-2}\) for the insulating SAM 1, and 1.07 \(\mu\)F cm\(^{-2}\) and 1.30 \(\mu\)F cm\(^{-2}\) respectively for the leaky SAMs 2 and 3. These values are in close agreement with the \(T\) values obtained from CNLS fits of the impedance data to the equivalent circuit II (Table 3). In addition to the semicircle, the complex plane
plots of the leaky SAMs exhibit straight lines at low frequencies due to ion diffusion into the films. A concomitant rise in $C'$ with decreasing frequency is observed at frequencies $<\sim1$ Hz (Fig. 3c). The maximum amplitudes of the relaxation peaks centered around 100 kHz in the Bode diagrams of $C'$ are approximately equal to one-half of the $C$ values at low frequency (indicative of a near homogeneous dielectric relaxation).

The complex plane and Bode plots of the real $\epsilon'$ and imaginary $\epsilon''$ parts of the complex relative permittivity $\epsilon$ (Fig. 3d-f) mirror those of the complex capacitance components. The $\epsilon'$ values at 0.1 Hz (Fig. 3e) immediately show that the insulating SAM 1 and the less leaky SAM 2 have nearly identical static dielectric constants, $\epsilon_{\text{SAM 1}} = 2.00$ and $\epsilon_{\text{SAM 2}} = 1.96$. The leakier SAM 3 has a higher dielectric constant, $\epsilon_{\text{SAM 3}} = 2.35$, due to the presence of ions and water molecules in the SAM.

Overall, the frequency dependence of the different dielectric parameters shows that leaky and insulating SAMs display differences at frequencies $<10$ Hz, especially between 1 and 0.1 Hz. Notably, the immittance data indicates that, depending on the degree of ion permeability, leaky and insulating SAMs do not always present significant differences in the static capacitance and dielectric constant. These properties are not reliable indicators of the ionic insulating quality of the SAM. Of the three measured parameters, $Z'$, $Z''$, and $\phi$, the most direct diagnostic indicator of ion
permeability is the phase angle $\phi$ at low frequencies. SAMs with a phase angle $\geq 89^\circ$ at frequencies of 0.1–1 Hz can be considered defect-free for practical purposes, meaning that current leakage at monolayer defect sites is negligible.

Effect of the $\text{CH}_3(\text{CH}_2)_n\text{S}$ Chain Length on the Dielectric Properties of the SAM

Representative impedance plots of gold electrodes modified with $\text{CH}_3(\text{CH}_2)_n\text{S}$ SAMs of $n = 9$, 11, 13, 15, 17, and 19 are presented in Fig. 4a-c. Here we consider only SAMs that exhibit $\phi$ of $\sim 89^\circ$ at 1 Hz and behave as ionic insulators to limit the alteration of the SAM dielectric response by current leakage at defect sites. A trend is not immediately apparent from the primary impedance data. By contrast, the corresponding capacitance plots (Fig. 4d-f) clearly resolve the chain length differences in the SAM dielectric characteristics. Both the diameters of the semicircles in the $C''-C'$ plots (Fig. 4d) and the $C'$ values at frequencies $< \sim 1$ kHz (Fig. 4e), where $C$ is largely independent of frequency, show outrightly the decrease of the static capacitance with increasing $n$ expected for an increasing layer thickness (eq 4). The chain length dependence observed in the Bode plots of $C$ extends to the Bode plots of $C'$, where the maximum peak amplitude decreases with increasing $n$.
The complex plane and Bode plots of $\epsilon'$ and $\epsilon''$ (Fig. 4g-i) show that $\dot{\epsilon}$ spans a narrow range.

Fig. 5a presents chain length dependent plots of the reciprocal of the capacitance of the SAM derived from the (i) fitted $T$ values ($\alpha = 0.991–0.994$), referred to as $C_T$, and (ii) $C$ values at 0.1 Hz, referred to as $C_{0.1\text{Hz}}$. First, $C_T$ ($1/C_T$) and $C_{0.1\text{Hz}}$ ($1/C_{0.1\text{Hz}}$) are statistically indistinguishable for a given $n$ (95% confidence level). Second, the reciprocal of the SAM capacitance varies linearly with $n$, indicating that the Au/S(CH$_2$)$_n$CH$_3$/electrolyte interface obeys the Helmholtz ideal capacitor model, as per eq 4. Dielectric constants were determined for each $n$ from $C_T$ and $C_{0.1\text{Hz}}$ using the SAM film thickness $d$ calculated assuming a 30° tilt from the surface normal of all-trans extended alkyl chains and a Au-S layer thickness of 0.19 nm.$^{40,41}$ Both capacitance parameters yield mean $\epsilon_{\text{SAM}}$ values that are the same (within error) for a given $n$ (Fig. 5b). $\epsilon_{\text{SAM}}$ increases linearly from $\sim2.01$ at $n = 9$ to $\sim2.20$ at $n = 15$ and tends towards a limiting value at longer chain lengths. $\epsilon_{\text{SAM}}$ is $\sim2.26$ at $n = 19$. Values of $\epsilon_{\text{SAM}}$ determined using electrochemical or optical methods range from 2.0 to 2.6 for CH$_3$(CH$_2$)$_n$SAu of $n \geq 9$.$^{23,37}$

$^{39,41,42}$
The optical (high-frequency) dielectric constant of CH$_3$(CH$_2$)$_n$SH liquids increases by $\sim$0.003 per CH$_2$ due to the higher dielectric constant of CH$_2$ ($\epsilon = 2.164$) versus CH$_3$ ($\epsilon = 1.399$). The linear variation of $\epsilon_{\text{SAM}}$ of $\sim$0.03 per CH$_2$ from $n = 9$ and 15 is however a factor of 10 greater, suggesting that the chain length dependence of $\epsilon_{\text{SAM}}$ stems from the supramolecular organization within the SAM. Theoretical studies indicate that the density of the surface-tethered alkyl chains influences the value of $\epsilon$. Surface IR spectroscopy measurements by Porter and coworkers reveal that the conformational disorder of the alkyl chains, in the form of gauche bond defects, progressively decreases with chain length, stabilizing at $n \gtrsim 15$, for which the CH$_2$ peak positions indicate that the chains are in a crystalline-like environment. The water contact angle $\theta$ (hydrophobicity) also shows an evolution of the SAM structure and associated interface with chain length (Fig. 6). The chain length dependence of $\theta$ mirrors that of $\epsilon_{\text{SAM}}$. $\theta$ plateaus at $109.6 \pm 0.3^\circ$ for $n \gtrsim 15$, signaling a constant SAM structure for the longer chains, in agreement with the findings of Chen et al. A greater conformational order should favor closer packing of the polymethylene chains in the SAMs and lead to a higher dielectric constant. The dielectric constants of SAMs formed from the longest-chain $n = 17$ and 19 approach the
value of 2.32 reported for high-density polyethylene. The observed increase in $\epsilon_{SAM}$ as a function of $n$ likely reflects an evolution of the alkyl chain order and packing density within the SAM.

In contrast to our findings, Góes et al. report a decrease in $\epsilon_{SAM}$ from $n = 7$ to $n = 11$ for leaky SAMs as the ionic permeability decreases with chain length. This clearly different chain length dependency highlights the need to use insulating SAMs for the electrochemical determination of the dielectric constant of the organic film.

Conclusions

We compared the non-faradaic electrochemical impedance response of the CH$_3$(CH$_2$)$_n$S-modified gold electrode with the mathematically-derived complex capacitance and relative permittivity to characterize the ionic insulating and dielectric properties of the SAM. The most unambiguous and direct indicator of the SAM leakiness is the measured phase angle at low frequencies. SAMs with a phase angle $\geq 89^\circ$ at frequencies of 0.1–1 Hz effectively behave as ionic insulators, whose complex plane plots
of the impedance and capacitance can be fit using a Helmholtz-type equivalent circuit. The real parts $C'$ and $\epsilon'$ respectively of the complex capacitance and relative permittivity derived from the imaginary part $Z''$ of the complex impedance at low frequency (0.1 Hz) directly yield the static interfacial capacitance and SAM dielectric constant, eliminating the need to model the Au/SAM/electrolyte interface with an appropriate equivalent electric circuit. The complex plane and Bode plots of the real and imaginary components $C'$ and $C''$ resolve outrightly the chain length dependence of the interfacial capacitance, unlike the analogous representations of the impedance components.

For ionic insulating SAMs, the reciprocal of the capacitance varies linearly with the number of methylene units in the CH$_3$(CH$_2$)$_n$S across the chain lengths investigated of $n$ = 9–19, indicating that the Au/SAM/electrolyte interface behaves as an ideal capacitor. The SAM dielectric constant determined from the capacitance using the Helmholtz model increases with $n$ and approaches the value reported for high-density polyethylene at $n \gtrsim 17$. The chain length dependence of $\epsilon_{\text{SAM}}$ is consistent with the evolution of the alkyl chain conformation and packing within the SAM indicated by a previous surface IR spectroscopy study$^{39}$ and our contact angle measurements. The variation of $\epsilon_{\text{SAM}}$ with $n$
has implications for SAM thicknesses measured by ellipsometry, in which a single dielectric constant is typically used for all chain lengths.\(^{39, 49, 50}\)

Our findings demonstrate that frequency-resolved capacitive ($C'$, $C''$) and permittivity ($\epsilon'$, $\epsilon''$) analyses are more effective than traditional representations and equivalent circuit modeling of the measured impedance at revealing the structure-related charging capacity and dielectric characteristics of an organic film-modified electrode/electrolyte interface. Future work will focus on characterizing the density and size of the defects in SAMs presenting different degrees of leakiness and non-Faradaic immittance signatures by using a redox probe in solution (Faradaic EIS).\(^{17, 51, 52}\)

**ACKNOWLEDGEMENTS**

This research was supported by NSERC (Discovery and Discovery Accelerator Supplement to A.B.). F.B.A. thanks the Tunisian Ministry of Higher Education and Scientific Research for a scholarship.
REFERENCES


Table 1. Impedance of Helmholtz- and Randles-type circuits\textsuperscript{53, 54}

Table 2. Conversion of the measured impedance to capacitance and relative permittivity\textsuperscript{10, 31, 38}

Table 3. Fitted results of the Randles circuit elements for CH\textsubscript{3}(CH\textsubscript{2})\textsubscript{11}SAu SAMs exhibiting different ionic insulating character
**Figure 1.** Schematic of the Au/S(CH$_2$)$_n$CH$_3$/aqueous electrolyte interface at an applied potential positive of the potential of zero charge. Equivalent circuits used to fit the impedance response of a defect-free SAM (I) and SAM presenting sites for ion permeation (II). $R_e$ is the electrolyte solution resistance, CPE is a constant phase element used to model the capacitance of the SAM-modified interface, and $R_{SAM}$ is the resistance to ion transport in the SAM. Complex plane impedance plots calculated using the equivalent circuits I and II and the parameters $R_e = 10 \ \Omega$, $T = 2 \times 10^{-7} \ \text{F s}^{\alpha-1}$, $\alpha = 0.993$, and $R_{SAM} = 5 \times 10^7 \ \Omega$. The lower highlighted inset is a zoom of the impedance data between 1 MHz and 1 Hz.

**Figure 2.** Impedance responses for CH$_3$(CH$_2$)$_{11}$SAu SAMs of differing ionic permeability. (a) Impedimetric complex plane plot. (b) Bode plot of the impedance magnitude $|Z|$. (c) Bode plot of $Z'$ and $Z''$. (d) Bode plot of the phase angle $\phi$. Impedance spectra were acquired at -0.185 V vs Ag/AgCl in 1.0 M NaClO$_4$(aq). Symbols are the experimental data and solid lines are the results of CNLS fits of the data using the equivalent circuit $R_e + R_{SAM}||$CPE.

**Figure 3.** Capacitance ($C', C''$) and relative permittivity ($\square', \square''$) spectra of CH$_3$(CH$_2$)$_{11}$SAu SAMs of differing ionic permeability. (a) Capacitive complex plane plot. (b) Bode plot of the real component $C$. (c) Bode plot of the imaginary component $C'$: dark
symbols are the raw data and light symbols are the data after subtraction of $R_e$. (d) Complex plane plot of the relative permittivity. (e) Bode plot of the real component $\epsilon'$. (f) Bode plot of the imaginary component $\epsilon''$. Symbols are the experimental data and solid lines are the results of CNLS fits of the impedance data using the equivalent circuit $R_e + R_{SAM}\parallel CPE$.

**Figure 4.** Immittance spectra of gold electrodes modified with CH$_3$(CH$_2$)$_n$S of $n = 9$, 11, 13, 15, 17, and 19. (a)–(c) Impedance, (d)–(f) capacitance, and (g)–(i) relative permittivity. Impedance spectra were acquired at -0.185 V vs Ag/AgCl in 1.0 M NaClO$_4$(aq). Symbols are the experimental data and solid lines are the results of CNLS fits of the impedance data using the equivalent circuit $R_e + R_{SAM}\parallel CPE$.

**Figure 5.** Chain length dependence of (a) reciprocal of the capacitance $C^{-1}$ ($C_T^{-1}$ or $C_{0.1\text{Hz}}^{-1}$) and (b) SAM dielectric constant $\epsilon_{\text{SAM}}$ determined from $C_T$ or $C_{0.1\text{Hz}}$ and the SAM thickness calculated for all-trans extended chains tilted by $30^\circ$ from the surface normal. Each data point is the mean value of at least 12 different SAMs. Error bars represent the
95% confidence intervals. Dashed line in (a) is a linear regression of the \( C_T^{-1} \) vs \( n \) data:

\[ r^2 = 0.9984. \]

Dashed line in (b) is a guide to the eye.

**Figure 6.** Comparison of the chain length dependencies of the static contact angle \( \theta \) of water and SAM dielectric constant \( \epsilon_{\text{SAM}} \). Inset shows the contact angle \( \theta \) of a sessile water drop on the SAM-functionalized gold surface. Each data point for \( \theta \) is the mean value of at least 4 different SAMs. Error bars represent the 95% confidence intervals.

Dashed line is a guide to the eye.
Table 1. Impedance of Helmholtz- and Randles-type circuits\textsuperscript{53, 54}

\[
Z'(\omega) = \frac{c_\alpha}{T \omega^\alpha} + R_e
\]

\[
Z'(\omega) = \frac{R_{\text{SAM}} (1 + (\omega TR_{\text{SAM}})^{\alpha} c_\alpha)}{1 + 2(\omega TR_{\text{SAM}})^{\alpha} c_\alpha + (\omega TR_{\text{SAM}})^{2\alpha}} + R_e
\]

\[
Z''(\omega) = -\frac{s_\alpha}{T \omega^\alpha}
\]

\[
Z''(\omega) = \frac{R_{\text{SAM}}(\omega TR_{\text{SAM}})^{\alpha} s_\alpha}{1 + 2(\omega TR_{\text{SAM}})^{\alpha} c_\alpha + (\omega TR_{\text{SAM}})^{2\alpha}}
\]

The angular frequency \(\omega = 2\pi f\), where \(f\) is the frequency in Hz. \(T\) and \(\alpha\) are the CPE parameter and exponent (eq 5). \(c_\alpha = \cos(\pi \alpha/2)\) and \(s_\alpha = \sin(\pi \alpha/2)\).
Table 2. Conversion of the measured impedance to capacitance and relative permittivity

<table>
<thead>
<tr>
<th>Complex quantity</th>
<th>Real part</th>
<th>Imaginary part</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ĉ(ω) = C(ω) + jC′(ω)</td>
<td>C'(ω) = (-\frac{Z'(ω)}{ω</td>
<td>Z(ω)</td>
</tr>
<tr>
<td>(\epsilon(ω) = \Box(ω) + j\Box'(ω))</td>
<td>(\epsilon'(ω) = \frac{Z'(ω)}{ω</td>
<td>Z(ω)</td>
</tr>
</tbody>
</table>

\(\omega = 2\pi f\), where \(f\) is the frequency in Hz. \(\epsilon_0\) is the permittivity of free space \((8.85419 \times 10^{-12} \text{ F m}^{-1})\), \(A\) is the electrode area, and \(d\) is the film thickness.
Table 3. Fitted results of the Randles circuit elements for CH$_3$(CH$_2$)$_{11}$SAu SAMs exhibiting different ionic insulating character

<table>
<thead>
<tr>
<th>SAM</th>
<th>$R_e$ / Ω cm$^2$</th>
<th>$R_{SAM}$ / MΩ cm$^2$</th>
<th>CPE</th>
<th>$\varphi$$_{1Hz}$</th>
<th>$\varphi$$_{0.1Hz}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.06±0.0</td>
<td>380±293</td>
<td>1.09±0.01</td>
<td>0.9912±0.000</td>
<td>89</td>
</tr>
<tr>
<td>2</td>
<td>3.07±0.0</td>
<td>12.9±0.3</td>
<td>1.09±0.00</td>
<td>0.9893±0.000</td>
<td>88</td>
</tr>
<tr>
<td>3</td>
<td>2.73±0.0</td>
<td>3.9±0.1</td>
<td>1.31±0.02</td>
<td>0.9976±0.000</td>
<td>87</td>
</tr>
</tbody>
</table>

The uncertainties in $R_e$, $R_{SAM}$, $T$, and $\alpha$ are from the CNLS fits of the impedance data.