Extensive ionic partitioning in interfaces that membranous and biomimetic surfaces form with electrolytes: Antitheses of the gold-electrolyte interface

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Abstract. Maxwell-Wagner modeling of electrical impedance measurements of tetradecane-electrolyte systems yielded three interfacial layers between the tetradecane layer and the bulk electrolytes of concentration ranging from 1-300 mM KCl whereas the gold-electrolyte system yielded only one layer. The conductivity and thickness for the surface layer were orders of magnitude different from that expected for the Gouy-Chapman layer and did not reflect dependencies of the Debye length on concentration. Conductivity values for the three layers were less than those of the bulk electrolyte but exhibited a dependency on concentration similar to that expected for the bulk. Thickness values for the layers indicate an interface extending ~10⁶ Å into the bulk electrolyte, which contrasts with the gold-electrolyte interface that extended only 20-30 Å into the bulk. Maxwell-Wagner characterizations of both interfaces were consistent with spatial distributions of ionic partitioning arising from the Born energy as determined by the dielectric properties of the substrates and electrolyte. The distributions for the membranous and silicon interfaces were similar but the antitheses of that for the gold interface.

1. Introduction
Silicon and gold have proven suitable substrates for supporting molecularly thin bio-sensitive surfaces in biosensors that on one side make contact with aquatic samples but on the other side provide connectivity to electronic devices that transduce the binding of targeted molecules in the samples. Such constructs introduce dielectric asymmetry not featured in biological systems in which a thin membrane separates two extensive aquatic phases (dielectric constant of $\epsilon_{\text{water}} = 79$) and perform the very binding events that the constructs are attempting to mimic. Essentially, the substrate in a biosensor replaces one of the aquatic phases, and its dielectric properties ($\epsilon_{\text{gold}} = \infty$ or $\epsilon_{\text{silicon}} = 11.5$) will influence differently the ionic concentrations in the single aquatic phase and the interfacial region where recognition of targeted molecules begins.

The magnitude and extent of such dielectric influences are characterized herein in a theoretical study and impedance measurements of electrolytes in contact with a tetradecane monolayer attached to silicon. These characterizations are compared with those in the literature of electrolytes in contact with gold substrates and bilayer membranes.
Figure 1

(a) 1mM KCl

(b) 300 mM KCl

(c) 1mM KCl

(d) 300 mM KCl

(e) Conductivity values (S/m)

(f) Conductivity values (S/m)

(g) Partition coefficients

Figure 1
2. Theory

Expressions for the spatial distribution of the Born energy [1] for an ionic species \( i \) of molecular radius \( r_i \) in a system comprised of a layer of thickness \( d \) and dielectric constant \( \varepsilon_x \) interposed between a medium of dielectric constant \( \varepsilon_1 \) on one side (\(-\infty<x<0\)) and a medium of dielectric constant \( \varepsilon_3 \) on the other, i.e. \((d<x<\infty)\) are given by:

\[
\mu_i^0 (\infty < x < r_i) = \frac{q_i^2}{16\pi \varepsilon_0 \varepsilon_x d} \left( \frac{2d}{r_i} - \frac{1}{(x/d)} + \vartheta_{3.1} \right)
\]

\[
\mu_i^0 (r_i < x < d - r_i) = \frac{q_i^2}{16\pi \varepsilon_0 \varepsilon_x d^2} \left( \vartheta_{2.1} \frac{2d}{r_i} + \sum_{n=0}^{\infty} \vartheta_{2,1,n} \frac{r_i^n}{(n-x/d)} - \frac{1}{(x/d)} - \sum_{n=0}^{\infty} \vartheta_{2,1,n} \frac{r_i^n}{(n+x/d)} \right)
\]

\[
\mu_i^0 (d + r_i < x < \infty) = \frac{q_i^2}{16\pi \varepsilon_0 \varepsilon_x d^2} \left( \frac{2d}{r_i} - \frac{\vartheta_{3.3}}{x/d} + \frac{\vartheta_{2,3}}{(x/d-1)} \right)
\]

where \( \vartheta_{3.1} \equiv \varepsilon_3 - \varepsilon_1 \), \( \vartheta_{3.2} \equiv \varepsilon_3 - \varepsilon_2 \), \( \vartheta_{1,2} \equiv -\vartheta_{2.1} \equiv \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + \varepsilon_1} \) (4)

and \( \varepsilon_x \) is dielectric permittivity in free space. These revert to expressions derived by Neumcke and Laüger [2] for a membrane separating two electrolytes when \( \varepsilon_1 = \varepsilon_3 = 79 \).

In the intermediate regions where the ion is partly in one medium and the other, the distribution can be approximated by the function:

\[
\mu_i^0 (x) = \frac{p_0 + p_2 x + p_2 x^2}{1 + q_1 x + q_2 x^2}
\]

where equating boundary energy and gradient values yields the polynomial coefficients.

The partition coefficient for ionic species \( i \) is defined so:

\[
\gamma_i \equiv \varepsilon - \mu_i^0 (\infty))/kT \approx \frac{C_i(x)}{C_i(\infty)}
\]

where the approximation applies in the absence of an electrical potential distribution when the partition coefficients determine the distribution of ionic concentrations, i.e. \( C_i(x) \) with respect to \( C_i(\infty) \).

Spatial distributions of the partitioning coefficients in the electrolytes \( (\varepsilon_x = 79) \) are shown in Figure 1(g) for a bilayer \( (d = 50 \text{ Å} \text{ and } \varepsilon_x = 3) \) separating two electrolytes, a tetradecane monolayer \( (d = 15 \text{ Å} \text{ and } \varepsilon_x = 2) \) separating silicon \( (\varepsilon_x = 79) \) and the electrolyte as well as a Stern layer \( (d = 8.08 \text{ Å} \text{ and } \varepsilon_x = 6) \) separating gold \( (\varepsilon_x = 100n\varepsilon_x) \) and the electrolyte.

3. Materials and Methods

A tetradecane monolayer was covalently attached to a \( \sim 15 \text{ mm square segment of n-type silicon (111) of resistivity } \sim 0.015\Omega \text{cm} \) using the technique described in detail previously [3]. Briefly, the segment was thoroughly cleaned and etched in deoxygenated ammonium fluoride producing a Si-H surface that was immediately reacted with 95% 1-tetradecene in a sealed vessel of nitrogen gas under ultraviolet illumination. The oxygen-purged atmosphere favored the reaction of H-C=H termini of tetradecane with the Si-H surface which yielded a layer of tetradecane rather than silicon dioxide. Gallium-indium eutectic was applied to the underside of the segment that formed a low-ohmic contact with the working electrode of an Inphaze 3-terminal characterization chamber shielded in a Faraday cage [4].

The chamber featured a spring and gearing mechanism for lowering a soft gasket of rectilinear cross-section onto the monolayer surface where it sealed a precisely defined ‘active’ area \( (1.81 \times 10^{-3} \text{ m}^2) \) without substantially distorting the surface at the gasket perimeter. KCl electrolytes of concentration 1, 3, 10, 30, 100 and 300mM were perfused in turn into the inner space of the chamber wetting the ‘active’ surface as well as the counter and reference electrodes. An Inphaze impedance spectrometer generated a spectrum of precise sinusoidal currents ranging in frequency from \( 10^2 \text{ to } 10^6 \text{ Hz} \) that were injected in turn through the electrolytes and monolayer via the counter and working electrodes. A recessed reference electrode and the working electrode connected to the inputs of an instrumentation amplifier (input impedance \( 10^{11} \Omega \)) sensed the voltage responses to the current stimuli. This amplifier and another simultaneously monitored the responses and stimuli that were buffered for transmission along low-impedance coaxial cables to the 24-bit ADCs of the spectrometer. The digitized data were transferred to a computer via a USB interface where the magnitude and phase of the impedances were calculated to respective resolutions of 0.002% and 0.001 degrees.
4. Results and Discussion

Impedance measurements of the tetradecane-electrolyte system are shown in Figures 1(a) and 1(b) for electrolyte concentrations ranging from 1 to 300mM. However, the measurements at high frequencies did not yield directly the known dielectric, geometrical and conductive properties of the bulk electrolytes such as are readily discernable from spectra of gold-electrolyte systems [5]. In this instance, the known properties for the electrolytes were introduced in the modeling as layer 0 in the Maxwell-Wagner models shown in Figures 1(c) and 1(d), the total impedance of which is given by;

\[
z_{MW} = \sum_{k=1}^{N_{MW}} \frac{d_k}{\sigma_k + j\omega k}
\]

where \(d_k\) denotes the thickness, \(\sigma_k\) the conductivity and \(\varepsilon_k\) the dielectric permittivity of the \(k^{th}\) of \(N_{MW}\) parallel layers. In contrast, the convergences of spectra at low frequencies in Figures 1(a) and 1(b) characterized the known concentration independent properties of the tetradecane monolayer and interfacial layers it forms with silicon, characterized in the models by layers 2 and 3, respectively.

The properties of layer 0 and those for layers 2 and 3 when required to fit the spectra, were then adjusted to obtain the least-squares-error fits of the models to the spectra also shown in Figures 1(a) and 1(b). Justification of the fits was based on \(\chi^2\)-statistics [6], which minimizes;

\[
Reduced - \chi^2 = \frac{\chi^2}{N - 2N_{MW}} \quad \text{where} \quad \chi^2 = \sum_{n=1}^{N} \left(\frac{\text{Mean}_n - f(\omega_n)}{\text{Error}_n}\right)^2
\]

in which \(f(w)\) denotes either the conductance or capacitance component of the model impedance, and Mean, Error, and \(\omega_n\) denote the mean, standard deviation and frequency, respectively, of the \(n^{th}\) of \(N\) measurements. Note that minimization of Equation (8) is countered by the number of Maxwell-Wagner layers, i.e. \(N_{MW}\), and provided justification for the inclusion or exclusion of layers 2 and 3.

Figure 1(f) shows that layer 0 features in models for all concentrations and the dependency of the conductivity of this layer on concentration is similar to that dependency of the electrolyte (layer 0 in Figure 1(e)) and the expected dependency of the Gouy-Chapman interfacial layer. However, the thickness values for layer 0 were \(\approx 10^6\) Å (e.g. see Figures 1(c) and 1(d)) which is orders of magnitude larger than Debye thicknesses for a Gouy-Chapman layer, and did not exhibit the expected dependency on concentration of the Debye thickness. Figure 1(e) shows that the conductivity values for layers 3 and 2 were orders of magnitude closer to those values for the electrolyte (layer 0) than those estimates for layer 0 and exhibited similar dependencies on concentration to the electrolyte and layer 0. The estimated thicknesses for layers 3 and 2 indicate that the tetradecane-electrolyte interface extended more than \(\approx 10^6\) Å into the electrolyte for concentrations less than 30 mM.

Layers 0, 3 and 2 characterize an interfacial region in which the conductivity (which is proportional to concentration) increases from values greater than that for the tetradecane monolayer (layers 3) to values less than that of the bulk electrolyte (layer 0). This interface extends many orders of magnitude further into the bulk electrolyte than the 20-30 Å for a gold-electrolyte interface with a concentration distribution consistent in form with that predicted by partitioning (Equations (1-6)) for this system shown Figure 1(g) and contrasting with that predicted for the gold interface reflecting constant bulk electrolyte properties. Figure 1(g) further illustrates the compatibility of silicon and membranous interfaces for recognizing, sequestering and binding biologically important molecules.

References
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