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Citation: Appl. Phys. Lett. 94, 043118 (2009); doi: 10.1063/1.3077605
View online: http://dx.doi.org/10.1063/1.3077605
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Time-dependent electrical double layer with blocking electrode

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(Received 27 November 2008; accepted 8 January 2009; published online 30 January 2009)

This paper deals with the experimental observation of time-dependent electrical double layer (EDL) in electrolyte. A potential-distance diagram is used to fully understand different stages in the formation of EDL. The influence of the thickness of the blocking layer and the ionic strength to the formation of EDL is discussed based on the equivalent circuit. With this simple method, it is found that in addition to Debye screening length, the frequency has to be considered if an alternating electric field is used to control the movement of charged biomolecules inside EDL. © 2009 American Institute of Physics. [DOI: 10.1063/1.3077605]

Using electric field to control the movement of biomolecules in aqueous solution has long been of particular interests as most biomolecules are in charged state and the charge density can be adjusted through adjusting the pH value of the solution. In the past years, many researches focused on the mutual electrostatic interactions of a large number of biomolecules in aqueous solution.1 However, such interaction can be complex because the strength and nature of these interactions are dependent on the physical and chemical properties of biomolecules as well as their spatial structures. Another way to manipulate the movement of biomolecules is through an external electric field, e.g., gel electrophoresis, which applies an electric field on the two sides of a gel separating molecules in aqueous solution.1 However, such interaction can be complex because the strength and nature of these interactions are dependent on the physical and chemical properties of biomolecules as well as their spatial structures. Another way to manipulate the movement of biomolecules is through an external electric field, e.g., gel electrophoresis, which applies an electric field on the two sides of a gel separating proteins on the basis of their mass.2 Unfortunately, it is not straightforward to use electric field in solution. When a solid electrode is immersed in an aqueous solution containing ionic species, the surface charges accumulated at the solid side cause a rearrangement of ions at the solution side, so-called the electrical double layer (EDL).3 EDL is usually a thin region with a large potential drop. The well-known Gouy–Chapman–Stern model defines EDL as two layers, the Stern layer and the diffuse layer, as shown in Fig. 1.4 The Stern layer can be further divided into two planes, the inner Helmholtz plane (IHP) and the outer Helmholtz plane (OHP). The former is the plane at the center of specifically adsorbed ions, and the latter is the plane cutting through the counterions at their position of closest approach.5 While ions inside the Stern layer are immobilized, they are mobile in the diffuse layer under the competition of electrostatic interactions and Brownian motion.

So far, studies of EDL are mainly on the static condition where only small perturbation in potential is considered. Linearized Poisson–Boltzmann equation is often used in this case, giving results with reasonable accuracy to experimental observations.5,6 The study of time-dependent EDL with large voltage perturbation, however, is less reported. Such study could be relevant to the possible health effect of electromagnetic wave on cells in the human body and has the potential of using electric field to modify the rate of protein adsorption to surfaces and the orientation of the adsorbed proteins.7 Linearized Poisson–Boltzmann equation is no longer valid in predicting time-dependent EDL; instead, the continuum equations together with Poisson’s equation are used in numerical modelings.8 There are also some obstacles present in the experimental study, e.g., the thickness of EDL is usually very thin, making it difficult to use most electrical probes. At steady state, the thickness of diffuse layer is given by the Debye screening length9

\[ \lambda_D = \frac{1}{\sqrt{4\pi l_B^2 \sum_i \rho_i z_i^2}} \]

where \(l_B\) is the Bjerrum length=0.7 nm and \(\rho_i\) and \(z_i\) are the density and valence of \(i\)th ion species. For an electrolyte at concentration of, say, 1 mM, \(\lambda_D\) is about 10 nm.

Here we use a method with simple instruments such as alternating electric source and oscilloscope to experimentally observe time-dependent EDL in electrolyte. Figure 2 shows the schematic of our setup. A 50 ml volume electrolytic cell ECDL was immersed in an electrolyte, and the potential was measured by oscilloscope. The potential-distance diagram is used to fully understand different stages in the formation of EDL.

FIG. 1. The Gouy–Chapman–Stern model for EDL. Two layers are defined in the solution side, the Stern layer and the diffuse layer. The Stern layer consists of two planes, the IHP and the OHP.

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made of polycarbonate has an orifice (diameter of 13 mm) on its sidewall. A blocking electrode made of polystyrene (PS) spin coated on highly doped n-type Si with an Al backing plate is the working electrode (WE). Blocking electrode is often used for studying both the electrochemical properties of solid film and the ion electrokinetic properties. PS was selected here because of its common occurrence and good dielectric property. The thickness of PS was varied from 3 to 257 nm, as measured by an ellipsometry (VB250, J. A. Woollam). WE was O-ring sealed to the electrolytic cell and in direct contact with the electrolyte through the orifice. A Pt counter electrode (CE) and a Ag/AgCl reference electrode (RE) in 3 M KCl solution were placed opposite of WE. In between WE and RE, two Pt electrodes were connected to an Tektronix TDS 340A oscilloscope (limit of ~1 mV). The distance between the four electrodes was the same, 15 mm. The idea of this method is that when a varied voltage is applied to WE, the voltage of a segment of the electrolyte can be measured, which can then be reflected to the formation of EDL.

At first we used WE with 257 nm thick PS film and a strong electrolyte, sodium chloride (NaCl) dissolved in distilled water (R > 18.5 Ω cm). It was noted that in order to effectively exert electrostatic force on charged biomolecules, Debye screening length given by Eq. (1) should be larger than the size of biomolecules (2–10 nm). This requires the solution ionic strength to be less than 1 mM. On the other hand, very low ionic strength increases solution resistance and may reduce the signal-to-noise ratio and detection limit. We therefore limited the ionic strength from 1 mM to 1 μM. An alternating double square-wave voltage with peak-to-peak value of 1 V was applied by a Newtronics function generator with a rise time of less than 0.5 μs [Fig. 3(a)].

Figure 3(b) shows the voltage measurement at 1 mM ionic strength of NaCl or [NaCl]. The curve displays a peak voltage immediately after the applied voltage. It then decays to the steady state at long time. When the applied voltage is reversed in the second half period, a symmetric response is formed in the curve. We found similar shape of curves in other measurements at other [NaCl]. The steady state current in all measurements was below 0.1 μA, implying no Faradaic reactions or hydrolysis of water molecules.

These curves can be understood from the potential-distance diagram, as shown in Fig. 3(c). In this figure, $\varphi_m$ is our measurement and $\varphi_s$ is the potential at the surface of PS film with respect to the ground state (RE). $\varphi_m$ is affected by the formation of EDL, as illustrated by three curves at different times $t_1$, $t_2$, and $t_3$ ($t_1 < t_2 < t_3$). Initially at time $t_1$, the applied voltage $\varphi_0$ at the electrode is distributed through the PS film and the electrolyte according to their dielectric properties. This immediately establishes an electric field in the electrolyte. Anions are attracted toward WE and cations are repelled away from WE under the influence of electrostatic interactions. At $t_2$, anions are accumulated at the surface of PS film, and the electric field in electrolyte will be reduced due to the screening effect of accumulated ions, i.e., EDL is formed. $\varphi_m$ therefore reduces during this period. Finally at $t_3$, EDL is fully developed and the applied potential is completely screened. $\varphi_m$ decays to the steady state, ~0 V. Overall, $\varphi_m$ measured at $t_1$, $t_2$, and $t_3$ are corresponding to the peak value, intermediate value in the decay region, and steady state value of the curve shown in Fig. 3(b). Our measurements can therefore effectively reflect the formation of EDL.

In a similar way we performed measurements with other blocking electrodes. We also define a parameter, the charging time $\tau$ of EDL, to characterize the decay rate of these curves. $\tau$ is calculated as the time required for the voltage $\varphi_m$ to decay from its peak value to 10% of peak value. The logarithmic plot of $\tau$ as a function of [NaCl] is shown in Fig. 4(a). Two features are observed from this plot. First, for most blocking electrodes, $\tau$ reduces as [NaCl] increases. Second, for blocking electrode with thick PS films, e.g., 257 nm, $\tau$ changes faster than that of thin PS films, e.g., 16 nm. For PS film less than 10 nm, $\tau$ is almost constant at 0.05 s regardless of [NaCl].
We explain the above observations using the Randle-type equivalent circuit shown in Fig. 4(b).\textsuperscript{11} In this figure, $C_{PS}$ and $C_{EDL}$ are the capacitance for PS film and EDL and $R_{PS}$, $R_{ct}$, and $R_E$ are the resistance for PS film, charge transfer, and electrolyte, respectively. Two assumptions are further made based on our experimental condition: (1) no Faradaic reactions, i.e., $R_{ct} \rightarrow \infty$ and (2) the resistance for PS film is very large because no leakage current is detected, i.e., $R_{PS} \rightarrow \infty$. The charging time $\tau$ for this equivalent circuit is therefore proportional to $R_E C_{eq}$ where $C_{eq}$ is the equivalent capacitance for $C_{PS}$ and $C_{EDL}$, given by

$$C_{PS} = \frac{A}{l_{PS}},$$

$$C_{EDL} = \frac{A}{l_{EDL}},$$

where $\varepsilon_0$ is the vacuum permittivity, $\varepsilon_1$ and $\varepsilon_2$ are the dielectric constant PS film and EDL, $l_{PS}$, and $l_{EDL}$ are the thickness for PS film and EDL, respectively.

We first consider the condition of a thick PS film, which gives $C_{PS} \ll C_{EDL}$. Under this condition, the charging process is dominated by PS film. This results in most potential drop across the PS film and a small value of $\varphi$, A simple calculation shows that even for the thinnest PS film used in our experiment (3 nm), the applied voltage will not break down the film.\textsuperscript{12} This corroborates that there is no current leakage at steady state. As $\varphi$ is small and NaCl is an electrolyte showing little specific adsorption, the length of EDL in Eq. (3) can be approximated determined by the Debye screening length. This gives a higher value of $C_{EDL}$ when [NaCl] increases. While $C_{PS}$ is almost independent on [NaCl], the dominance of $C_{PS}$ in the charging process at higher [NaCl] is enhanced. We therefore expect a simple charging process of PS film and the charging time $\tau$ changes with $R_E$, which reduces as [NaCl] increases. The nonlinearity at low [NaCl] may be due to the polarization of water or the dissociation of CO$_2$ from external environment, which induces extra ions such as H$_3$O$^+$, HCO$_3^-$, and CO$_3^{2-}$ in solution.

The influence of [NaCl] on $\tau$ is different for thin PS film where the condition of $C_{PS} \ll C_{EDL}$ is violated. In this case, the charging process is determined by the formation of EDL instead of the PS film. As large potential drop is expected across EDL, the approximation of using Debye screening length for $C_{EDL}$ is no longer valid. When [NaCl] increases, $\tau$ will be determined by two competitive processes. On one hand, $C_{EDL}$ becomes larger for most electrodes at higher [NaCl], as shown by previous researchers.\textsuperscript{11,13} On the other hand, $R_E$ reduces at higher [NaCl] due to higher density of charge carriers. A balance between the two processes results in a much slower decay rate of $\tau$ when [NaCl] increases. This is consistent with our observation in Fig. 4(a), where $\tau$ is about 0.05 s for PS film less than 10 nm. Nevertheless, a more rigorous solution to the changes in $\tau$ would be numerical modeling with proper boundary conditions.\textsuperscript{8}

In summary, we experimentally observed time-dependent EDL with PS blocking electrode. Different stages of EDL were understood with the aid of the potential-distance diagram. Two conclusions were made from the plot of the charging time $\tau$ as a function of [NaCl] at different PS films. First, $\tau$ was determined by PS film for thick blocking layers and by the formation of EDL for thin blocking layers. Second, the time required to fully develop EDL with large potential drop was about 0.05 s. This time has to be fulfilled if an alternating electric field is used to control the movement of charged biomolecules.

The authors acknowledge Dr. Neil Nosworthy and Dr. Huiying Yang for helpful discussion. This project is financially supported by MOE and A*STAR, Singapore, under Grant No. 0421010080.