

# Streaming Zeta Potential Measurements Of Surface-Bound Organosilane Molecular Species

D.S. Wright, B.S. Flavel and J.S. Quinton\*

Smart Surface Structures Group

School of Chemistry Physics and Earth Sciences

Flinders University, Sturt Road, Bedford Park, Adelaide SA 5001

\*Corresponding Author, Email: Jamie.Quinton@Flinders.edu.au

Telephone: (08) 82013994

**Abstract**— Surface modification is frequently adopted to alter a given objects ability to fit to its purpose. One such method is through modification by adsorbed molecular species, such as for self-assembled monolayers (SAMs). In this paper we present data showing how Streaming Zeta measurements can be used as a complimentary technique to Atomic Force Microscopy for characterisation of a surface that has been subject to molecular modification.

**Keywords:** *Streaming Zeta Potential, surface modification, self-assembled monolayer, organofunctional silane films.*

## I. INTRODUCTION

When fluid flows across a solid surface, the surface of the solid may become charged. Ions of opposite charge within the liquid medium are attracted to the surface in order to neutralize the surface charge creating what is commonly referred to as an electric double layer (EDL). The strength and polarity of the EDL is represented by the parameter known as the Zeta potential [1]. The Zeta potential is a useful parameter for determining electrokinetic chemical properties of both pristine and modified surfaces.

Experimentally, the Zeta potential for a solid surface is measured via a streaming potential, which occurs by forcing fluid through a channel. The channel is comprised such that two of the solid surfaces to be studied exist in a parallel plate arrangement. Ions move in the direction of fluid flow setting up a streaming current. This accumulation of charges at one end of the channel causes a build up of charge which forms a potential difference between either ends of the channel. The potential difference caused by this build up of charge creates a leak current in the opposite direction of fluid flow due to ion diffusion and electro-osmotic flow. A steady state is achieved when the back current is equal to the streaming current and it is at this point where a measurement of the Zeta potential is taken [2].

Traditionally the calculation of the Zeta potential is achieved through the use of the well known Helmholtz-Smoluchowski (H-S) equation (1) which has been extended from use in capillary system to parallel plates [3].

$$\zeta = \frac{\Delta E}{\Delta P} \frac{\eta \lambda_0}{\epsilon_0 \epsilon_r} \quad (1)$$

In equation 1,  $\Delta E$  is the streaming potential,  $\Delta P$  is the applied pressure that causes the hydrodynamic flow,  $\epsilon_0$  is the permittivity of free space  $\epsilon_r$  is the dielectric constant for the streaming solution,  $\eta$  is the viscosity of the streaming solution,  $\lambda_0$  is the electrical conductivity of the streaming solution and  $\zeta$  is the Zeta potential [4]. Experimentally, the Zeta potential is measured by applying a pressure gradient across the channel and measuring the resulting potential. All of the parameters on the left hand side of equation 1 are able to be directly calculating for each particular streaming solution thus allowing for easy calculation of the Zeta potential.

The Zeta potential is pH dependent due to the acid/base properties of the oxide surfaces [5] as well as affecting various parameters in equation 1. Therefore the Zeta potential is typically quoted as a function of pH for a particular surface under investigation. The pH at which the surface charge is zero is called the point of zero charge (pzc) and is typically used to quantify or define the electrokinetic properties of a surface.

## II. CONTACT ANGLE MEASUREMENTS

Commercially available glass microscope slides were cut into square samples 20x20mm. The glass slides were initially cleaned in Deionised (DI) water (resistivity greater than 18.2 M $\Omega$ cm<sup>-1</sup>) then placed in a 4:1 solution of sulphuric acid (Chem Supply 80%) and hydrogen peroxide (Chem Supply) (piranha solution) at a temperature of 80°C for a period of 30 minutes, in order to remove any organic contaminants present on the surface. The glass samples were then rinsed and stored in DI water. Prior to use glass slides were thoroughly dried under nitrogen. By thoroughly cleaning the glass, a thin, clean oxide layer with a high density of silanol groups (Si-OH) can be obtained. It is these silanol groups which provide the point of attachment for silanization reactions. The presence of a high surface density of -OH groups was verified by contact angle measurements (Figure 1), cleaned glass slides exhibiting a

water contact angle of  $0^\circ$  indicating a highly hydrophilic surface.

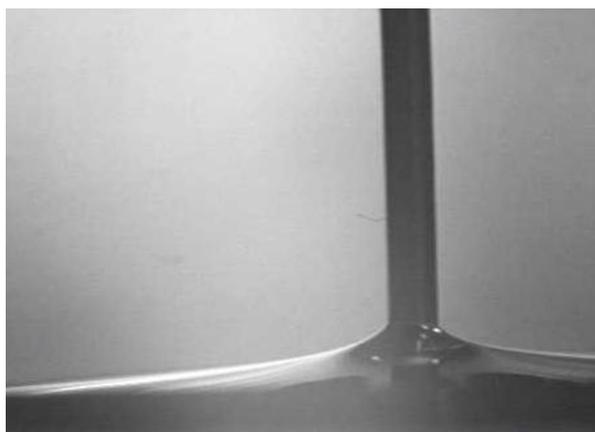


Figure 1. Contact angle measurement of glass microscope slides cleaned in piranha solution, indicating a high degree of hydroxylation.

### III. ZETA POTENTIAL OF GLASS MICROSCOPE SLIDE

The clean glass slides were assembled into a purpose built sample cell to create a parallel plate configuration. Streaming potential measurements were performed in a moderate pH range. Phosphate buffers created in DI water were used in a pH range of 4 to 10 in order to monitor the Zeta potential as a function of pH for the glass slides. A plot of the Zeta potential versus pH for the liquid glass interface can be observed in Figure 2.

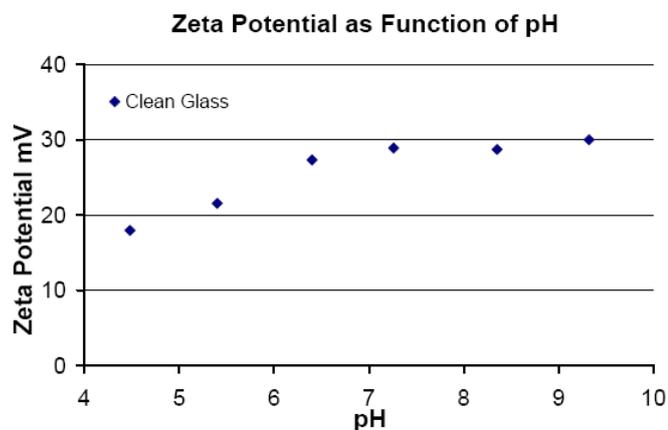


Figure 2. Zeta potential versus pH for clean glass microscope slides indicating no observable pzc.

It is evident from Figure 2 that a point of zero charge (pzc) is not achieved over the pH range investigated. However this is not completely unexpected as work done by Gu et al.[1] on calculating the Zeta potential of glass microscope slides revealed that even at a pH as low as 2.68 a pzc wasn't observed.

### IV. ORGANOFUNCTIONAL SILANE COATINGS ON GLASS

Silanisation of the glass slides was used to see if altering the surface properties had a noticeable effect on the electrokinetic properties of the surface. Octadecyltrichlorosilane (Aldrich 90+% purity) or OTS was

the silane chosen to alter the surface. The glass slides were coated in a 0.5% (v/v) solution of OTS in hexadecane (99% sigma) for approximately 5 minutes, ultrasonicated in chloroform for 10 minutes and then dried under a stream of nitrogen. A contact angle of  $116^\circ$  was measured for the coated glass slides, which is in agreement with other research groups [6], suggesting a highly ordered monolayer of OTS had been formed.

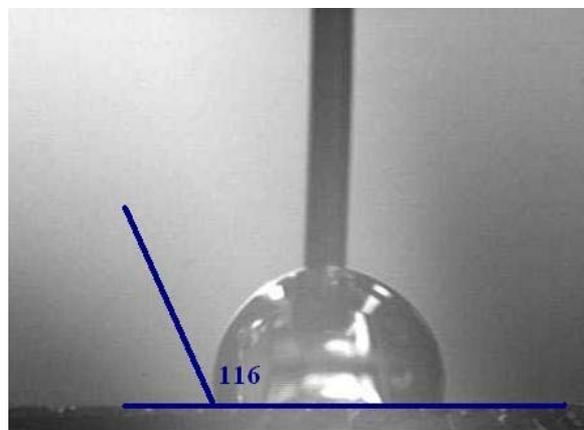


Figure 3. Contact angle measurement of OTS monolayer present on the glass microscope as indicated by a highly hydrophobic surface.

Transmission infra red (IR) spectroscopy was used to indicate the presence of alkane groups on the surface. Two prominent peaks can be seen at  $2918\text{cm}^{-1}$  and  $2850\text{cm}^{-1}$ , which are associated with the symmetric and asymmetric stretching modes of  $\text{CH}_2$  groups on the silane alkane chain [7]. The position of these peaks indicates that a well ordered crystalline monolayer of OTS has been formed [6].

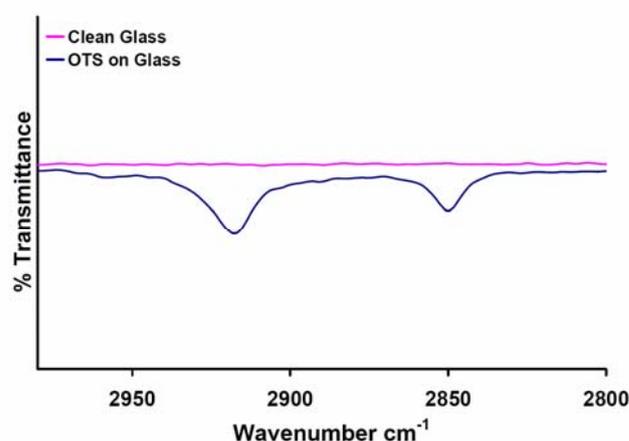


Figure 4. Infrared spectra of clean and silanised glass showing the presence of C-H bonds associated with alkane chain of the silane.

Atomic Force microscopy (AFM) was used to give further indication of surface coverage. AFM images were taken in air with a multimode-head and Nanoscope IV controller, Digital Instruments, Veeco, Santa Barbara, operating in tapping mode. Commercially available silicon cantilevers (FESP-ESP) with fundamental resonance frequency between 70-85 KHz were used. Figure 4 shows an AFM image of OTS coated glass

wherein it can be seen that OTS has formed a densely packed layer on the glass.

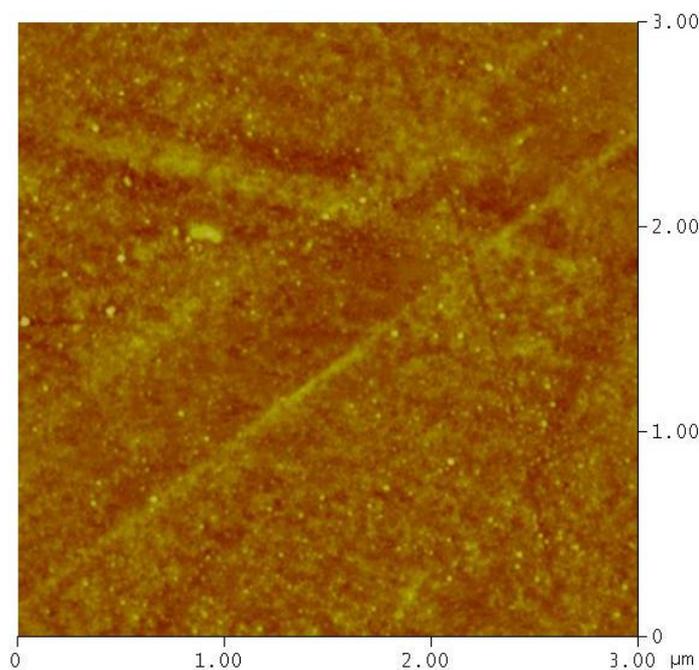


Figure 4. AFM image of OTS monolayer on glass indicating a large degree of surface coverage.

Given the strong evidence from IR spectroscopy, AFM imaging along with contact angle measurements indicate that OTS was present on the surface in a monolayer coverage. Streaming potential measurements were once again performed on the surface over the same pH range as that for the non-silanised glass slides. All of the experimental parameters were kept constant in order to observe the effect that the silanisation treatment had on the surface. A plot of Zeta potential versus pH can be seen in Figure 5 for both the clean microscope slides and the silanised glass slides allowing for easy comparison.

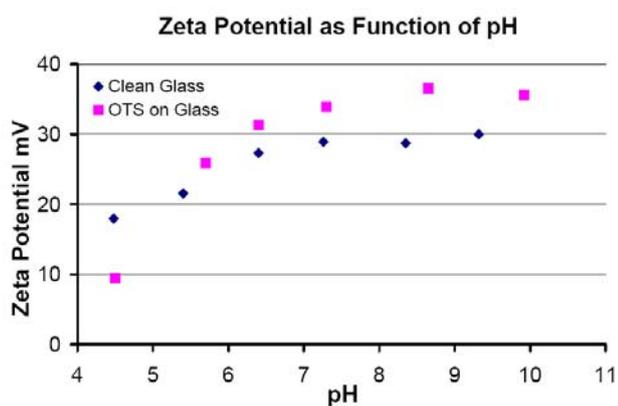


Figure 5. Zeta potential as a function of pH for clean glass and silanised glass showing a slight increase in Zeta potential at elevated pH

A typical feature commonly noticed in plots of Zeta potential versus pH is that the rate of change of Zeta potential as a function of pH is most rapid around the isoelectric point (IEP) indicating that a slight deviation from a neutrally charged surface has a dramatic effect on the Zeta potential. This result is similar to that noticed when performing an acid based titration with a strong acid and base. When the solution is near its stoichiometric end point (neutral pH) any slight addition of either an acid or base will dramatically alter the pH of the solution. Another key feature of plots of Zeta potential versus pH is that as the pH gets further and further away from the IEP the Zeta potential plateaus. A plateau is observed for both the clean glass slide along with the silanised glass slide at a pH of 8. Also of note also is that a pzc is not observed for either sample, however the Zeta potential profile for both samples is noticeably different.

## V. CONCLUSION

This work demonstrate that streaming Zeta potential is useful for charaterising modified surfaces. However, the system chosen in this instance has a pzc that occurs below the lower working limit of the instrument. However from the data that has been presented the Zeta potential for the two different surfaces is noticeably different. Current investigations in our laboratory are examining the use of a silane with a terminal amine group (which will produce a pzc above 10) to functionalise the glass surface. Such a choice in silane is expected to significantly enhance the sensitivity of the technique and further demonstrate its applicability.

## REFERENCES

- [1] Gu, Y. and D. Li, *The [Zeta]-Potential of Glass Surface in Contact with Aqueous Solutions*. Journal of Colloid and Interface Science, 2000. **226**(2): p. 328-339.
- [2] Hunter, R.J., *Zeta Potential in Colloid Science : Principles and Applications*. 1981: London : Academic Press 1981.
- [3] Elimelech, M., W.H. Chen, and J.J. Waypa, *Measuring The Zeta (Electrokinetic) Potential of Reverse Osmosis Membranes by a Streaming Potential Analyzer*. 1994. **95**(3): p. 269.
- [4] Fievet, P., et al., *Determining the Zeta-Potential of Plane Membranes From Tangential Streaming Potential Measurements: Effect of the Membrane Body Conductance*. 2003. **226**(1-2): p. 227.
- [5] Jayaweera, P. and S. Hettiarachchi, *Determination of Zeta potential and pH of zero charge of oxides at high temperatures*. Review of Scientific Instruments, 1993. **64**(2): p. 524-528.
- [6] D.K. Aswal, S.L., D. Guerin, J.V. Yakhmi, D. Vuillaume, *Self-assembled monolayers on silicon for molecular electronics*. Analytica Chimica Acta, 2005. **In Press**.
- [7] Morales-Cruz, A.L., et al., *Self-assembled monolayers and chemical derivatization of Ba<sub>0.5</sub>Sr<sub>0.5</sub>TiO<sub>3</sub> thin films: Applications in phase shifter devices*. Applied Surface Science, 2005. **252**(4): p. 981-995.