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Supporting Information for Potential Dependence of Surfactant Adsorption at the Graphite Electrode / Deep Eutectic Solvent Interface

Katharina Häckl,¹ Hua Li,² Iain Aldous,³ Terrence Tsui,² Werner Kunz,¹ Andrew P. Abbott³ Gregory G. Warr,⁴ and Rob Atkin^{2,*}

¹ *Institute of Physical and Theoretical Chemistry, University of Regensburg, Universitätsstraße 31, D-93053 Regensburg, Germany.*

² *School of Molecular Sciences, The University of Western Australia, 35 Stirling Highway, Perth, WA 6009, Australia. E-mail: Rob.atkin@uwa.edu.au*

³ *Materials Centre, Department of Chemistry, University of Leicester, Leicester LE1 7RH, UK.*

⁴ *School of Chemistry and University of Sydney Nano Institute, The University of Sydney, NSW 2006, Australia*

S1 Experimental Section

DESS were prepared by mixing choline chloride (Sigma-Aldrich, $\geq 98\%$) with ethylene glycol (Sigma-Aldrich, $\geq 99.8\%$) and glycerol (Sigma-Aldrich, $\geq 99\%$) in a 1:2 ratio and stirring at 40 °C until a homogenous clear liquid was formed. Mixtures were dried in vacuum for 24 h. Water contents of 0.7 wt% for ChCl-EG and 0.8 wt% for ChCl-Gly were determined by Karl Fischer titration. Sodium dodecylsulphate (SDS) and cetyltrimethylammonium bromide (CTAB) were purchased from Aldrich and used as received.

AFM force measurements and imaging were performed using a Nanoscope IV multimode atomic force microscope (Bruker Instruments). The setup consisted of a standard silicon tip (NSC36, MikroMasch) with a radius of 32.5 nm and a spring constant between 0.2 and 0.8 N/m, a PTFE O-ring and an AFM liquid cell. The 10x10x2 mm HOPG surface of ZYB quality were purchased from TipsNano with a mosaic spread of $0.8 \pm 0.2^\circ$. Prior to use, the tip was rinsed with Millipore water

and ethanol (analytical grade), dried and placed in a UV-ozon cleaner for at least 20 minutes. The graphite surface was prepared by cleaving the top layer with adhesive tape. An Autolab potentiostat was used to apply potential to the graphite surface. Each system was evaluated at open-circuit potential (OCP), $OCP \pm 0.5$ V and $OCP \pm 0.75$ V. Before each measurement, the system was allowed to reach equilibrium for at least 10 min. Deflection images of the aggregates were taken in soft contact mode by setting the deflection setpoint to a precontact region when scanning the surface.^[22,30,31] The deflection image shows how the AFM cantilever bends as it passes over the sample. It is used to determine how the z piezoelectric must move to maintain a constant tip-sample force during contact mode AFM measurement. The amount of the z piezo moves is used to form the sample height image. Scanning angles and sizes were varied to ensure the features in images are real. repeat images were obtained on different days to ensure reproducibility. Measurements were conducted at room temperature of 22 ± 1 °C. For systems and potentials where surface aggregation occurred, characteristic features were evident within 30 minutes of the solution was passed into the AFM cell.

The spacing of periodic surface features was determined by power spectral density (PSD) analysis using the Bruker NanoScope Analysis software. Measuring periods of images where the scanning angle is not perpendicular to the aggregate symmetry axis results can lead to errors. Due to this, only images with deviations smaller than $\pm 5^\circ$ from perpendicular were analysed. The aggregate periods given in this work are formed by the average of at least 3 measurements. Errors were < 0.1 nm.

Cyclic voltammetry measurements were performed using an Autolab PGSTAT20 software-controlled potentiostat. The measurement system included a silver reference electrode, a platinum sheet as the counter electrode and a HOPG working electrode. Cyclic voltammograms were recorded with a scan rate of 10 mV/s in DESs in presence and absence of certain amounts of surfactants.

S2 AFM Images

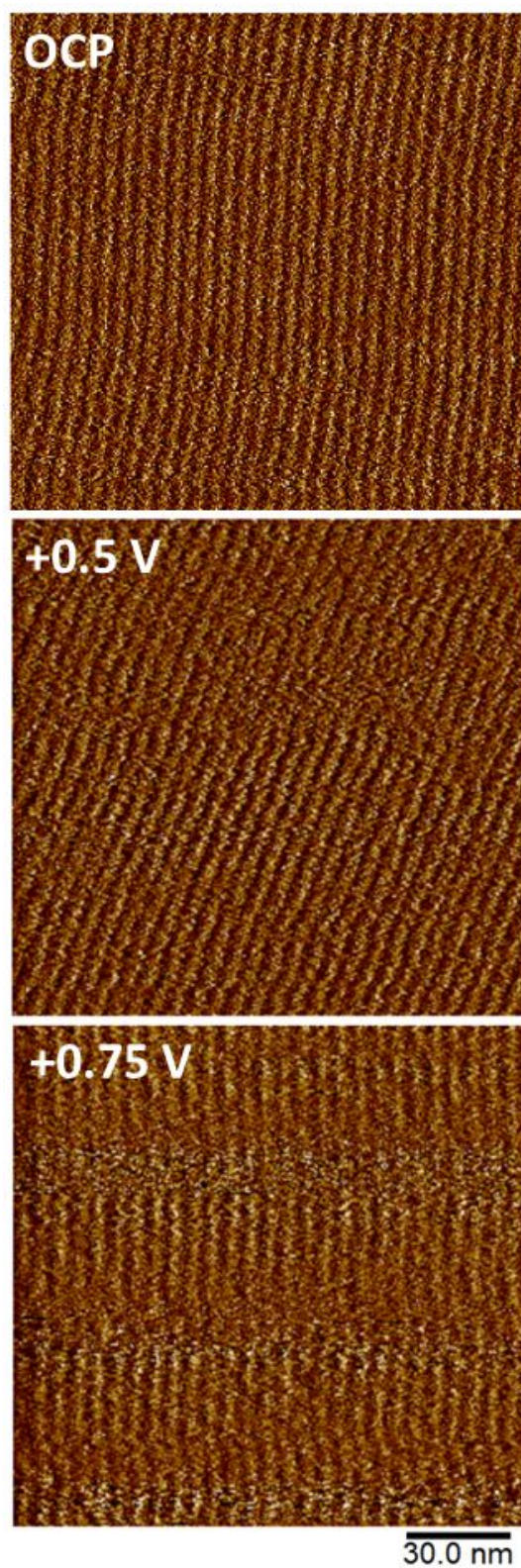


Figure S1. AFM deflection images for the graphite- ChCl-EG interface with 25 mM SDS at OCP, 0.5V and 0.75V.

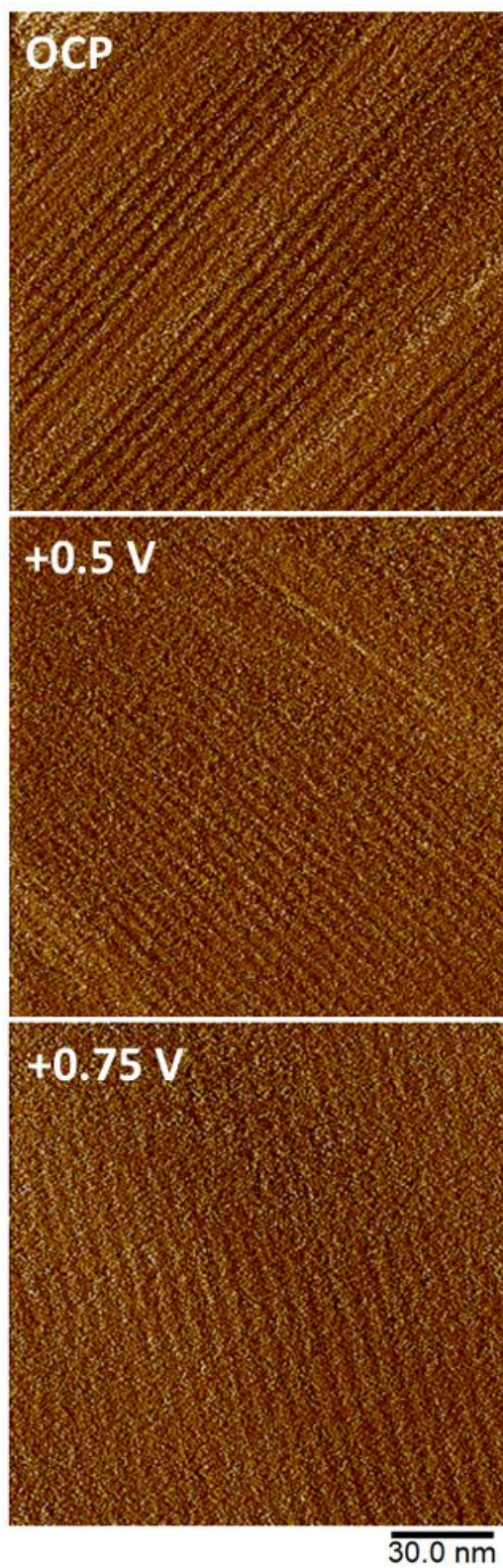


Figure S2. AFM deflection images for the graphite - ChCl-Gly interface with 10 mM SDS at OCP, 0.5V and 0.75V.

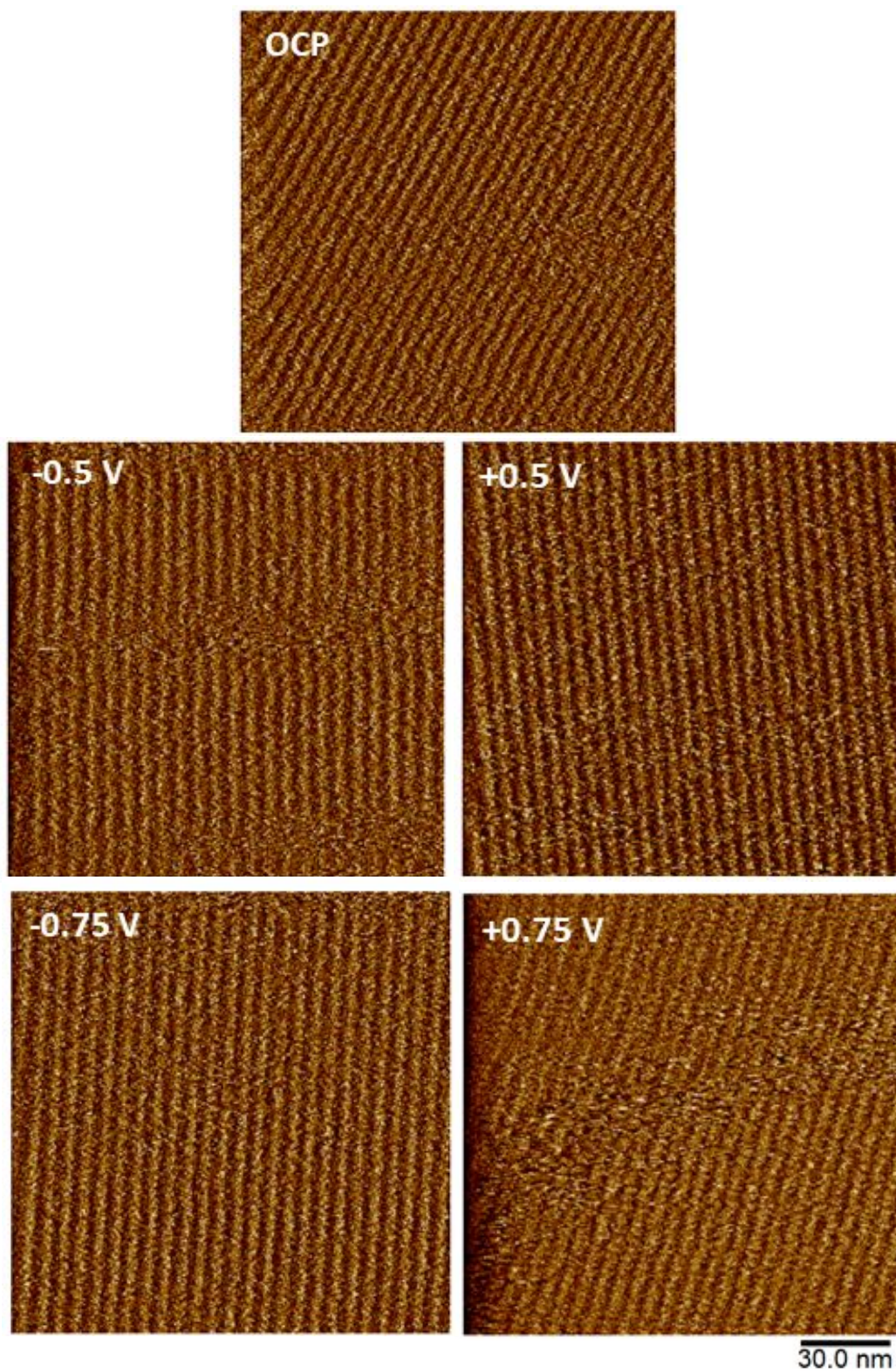


Figure S3. AFM deflection images for the graphite - ChCl-Gly interface with 2.5 mM CTAB at -0.75V, 0.5V, OCP, 0.5V and 0.75V.