

SUPPORTING INFORMATION

Real-Space Investigation of Electrical Double Layers. Potential Gradient Measurement with a Nanometer Potential Probe

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The potential and potential gradient curves measured at different linear translational speeds of the probe

Figure S1 compares the potential (V_{pr}) and potential gradient (dV_{pr}/ds) curves simultaneously obtained in the distance-modulation experiments conducted at different linear translational speeds (3-20 nm s⁻¹) of the probe. The normalized potential profiles converted from the experimental dV_{pr}/ds curves are also shown. The V_{pr} curves (top) showed that the hysteresis effect became stronger as the probe retracted at a faster linear speed. The dV_{pr}/ds curves (middle), however, indicated that the width of the bell-shaped profile was rather unaffected by the scan speed. The area under the dV_{pr}/ds curve measured during the retract motion gradually decreased as the profiling speed increased, which, according to eq. (3), indicated that R_{misc} was smaller during the retract than during the approach. As a result, the converted V_{pr} curves had different heights for the approach and retract scans, but they were displayed in the normalized scale $[(V_{pr} - V_{bulk})/(V_{WE} - V_{bulk})]$ in the figure for the purpose of graphical clarity in comparing their relative width only. The normalized potential curves (bottom) show approximately the same profile width, within the experimental accuracy, little affected by the speed and direction of the linear scan motion of the probe.

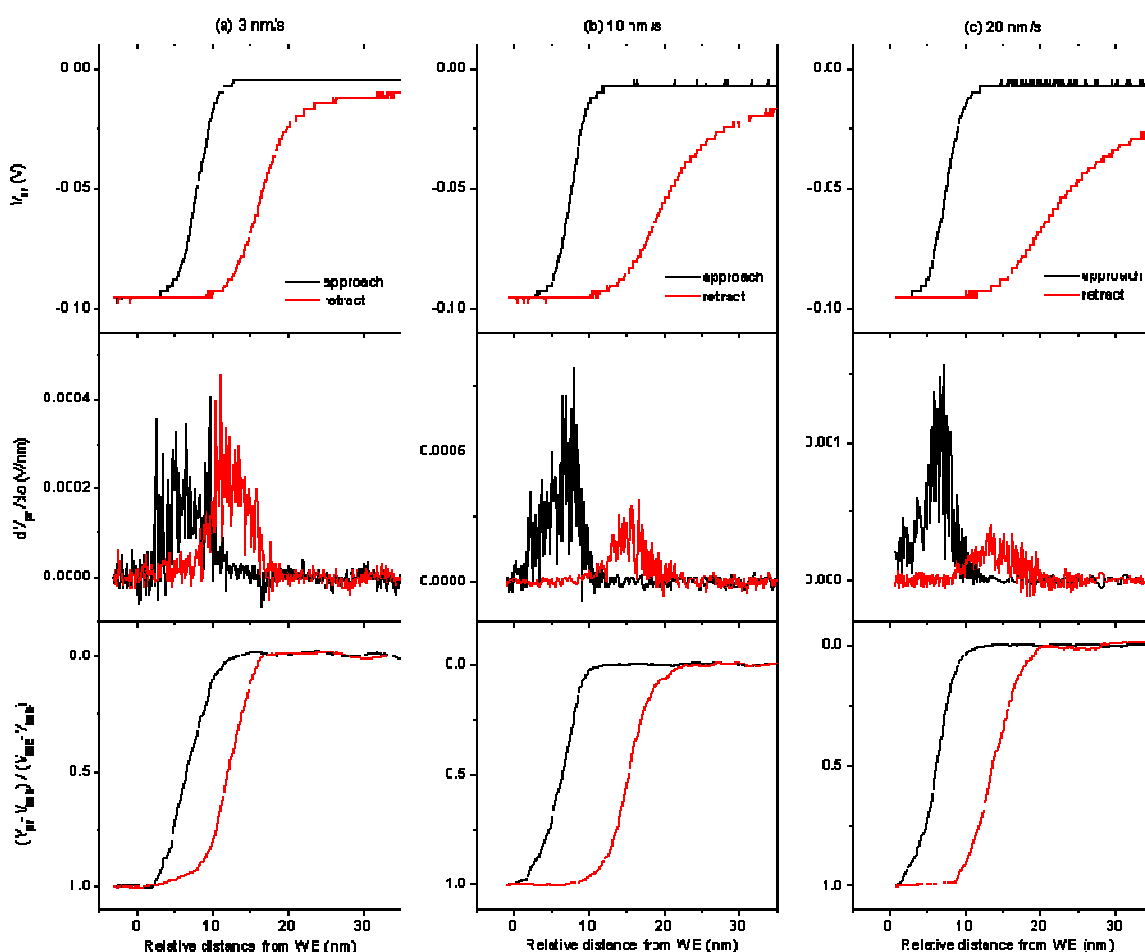


Figure S1. The potential (V_{pr} ; top) and potential gradient (dV_{pr}/ds ; middle) curves measured in a 1.0 mM NaClO_4 solution at different linear scan speeds of the probe. The normalized potential profiles $[(V_{pr} - V_{bulk})/(V_{WE} - V_{bulk})]$ converted from the experimental dV_{pr}/ds curves are shown in the bottom panels. The probe scan speed was (a) 3 nm s^{-1} , (b) 10 nm s^{-1} , and (c) 20 nm s^{-1} . The probe oscillation frequency was 30 Hz

and the oscillation amplitude (Δs_{rms}) was 0.25 nm. V_{WE} was -0.10 V with respect to the

ground (E_{WE} was 0.0 V vs. gold quasi-RE, which corresponded to $\sim 0.33 \text{ V}$ vs. Ag/AgCl). The size of the gold probe was 100 nm in radius assuming a disk-shaped surface. The

dV_{pr}/ds curves had high frequency noises due to a fast time constant (0.03 s) of the lock-in amplifier, which overshadowed smaller periodic ripples due to probe oscillation such as those appearing in Figs. 2 and 5 in the manuscript.