

Effect of Conformational Order of the Hydrocarbon Chains on the Rates of Electron Tunneling Across Alkanethiol Monolayers on Mercury Electrodes and in Hg-Hg Tunneling Junctions

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We have investigated the influence of the order-disorder transition on the rate of electron transfer across alkanethiolate monolayers and bilayers using the Hg-Hg tunneling junction method. The latter involves two suspended mercury drops coated with alkanethiolate monolayers which are brought into contact. Using potentiodynamic and ac impedance methods, we have shown that the initial largely all-trans structure of the bilayer becomes disordered with time as a result of the van der Waals and coulombic forces squeezing the junction. To characterize the strength of the electronic coupling across these junctions, we measured the decay constant  $\beta$  for native bilayers featuring a largely all-trans conformation and for more disordered junctions. The tunneling coefficient for native bilayers was obtained using fast-scan ( $500 \text{ V s}^{-1}$ ) current-voltage experiments and yielded  $\beta = 1.29$  per  $\text{CH}_2$  ( $1.0 \text{ \AA}^{-1}$ ). Impedance measurements were used to investigate properties of the disordered junctions. Electron tunneling resistance and the junction capacitance were measured simultaneously. The plot of the logarithm of junction resistance measured at zero voltage bias versus thickness gave  $\beta = 1.6 \text{ \AA}^{-1}$ . A similar effect of increased tunneling decay constant was observed in

electrochemical experiments with a single Hg drop working electrode coated with two component alkanethiolate monolayers. Mixed monolayers of two dissimilar alkanethiols ( $\text{C}_n\text{H}_{2n+1}\text{SH} / \text{C}_m\text{H}_{2m+1}\text{SH}$ ;  $n = 9, 10$  and  $m = 14, 16, 18$ ) were assembled to induce disorder in otherwise well behaved barrier film. Electron tunneling between the  $\text{Fe}(\text{CN})_6^{3-}$  in the electrolyte solution and Hg was measured as a function of the mole fraction of the shorter component in the monolayer film. A detailed discussion of the influence of monolayer disorder on the kinetic parameters of  $\text{Fe}(\text{CN})_6^{3-}$  reduction will be presented.