

Long-Range Electron Transfer through Monolayers and Bilayers of Alkanethiols in Electrochemically Controlled Hg-Hg Tunneling Junctions.

Roger L. York and Krzysztof Slowinski

Department of Chemistry and Biochemistry, California State University Long Beach, 1250 Bellflower Boulevard, Long Beach, CA 90840-3903

The rates of electron tunneling through monolayers and bilayers of alkanethiols self-assembled in a potentiostatically controlled Hg-Hg junction are reported. An alkanethiolate monolayer is formed in-situ on either of the Hg drops via oxidative adsorption. In this approach the mercury electrode is held at a potential at which the formation of a monolayer is allowed and a fresh Hg drop is rapidly extruded at the tip of a glass capillary. The rapid current increase and then decay to zero corresponds to the formation of an alkanethiolate monolayer as described in earlier reports. The extrusion of a second Hg drop, performed at a more negative potential, results in a cathodic *i-t* transient consistent with the electrical double-layer charging in the absence of an adsorbed monolayer of alkanethiols. Subsequently, the Hg drops are brought into contact using micromanipulators. The junction formation is instantly followed by the flow of a steady-state tunneling current between the two electrodes. Using an analogous approach the tunneling current through an in-situ formed alkanethiol bilayer can also be measured. A plot of the logarithm of the tunneling current density vs. the total number of carbon atoms in each junction yields identical tunneling coefficients (ca. 1 per methylene unit) for monolayers and bilayers of alkanethiols. Careful examination of the tunneling data indicates that the solvent and ions are ejected from the junction area. This conclusion is not surprising in view of: (i) strong adhesion between a hydrophobic monolayer and a hydrophobic Hg surface (or a second monolayer), (ii) attractive dispersion forces between two Hg drops separated by a very short distance, (iii) electrostatic attraction of two drops due to the bias voltage. The tunneling current recorded for a bilayer of 1-octanethiol or 1-nonanethiol is ca. 2 fold larger than a corresponding tunneling current recorded for monolayers of 1-hexadecanethiol or 1-octadecanethiol respectively. This is a surprising effect since the geometric thickness of a bilayer of alkanethiol is larger than the thickness of a monolayer containing the same number of carbon atoms. We explain

this result in terms of very weak electronic coupling across the non-covalent molecule/electrode interface.