Utilizing Self-Assembled Monolayers to Understand Interfacial Electron Transfer

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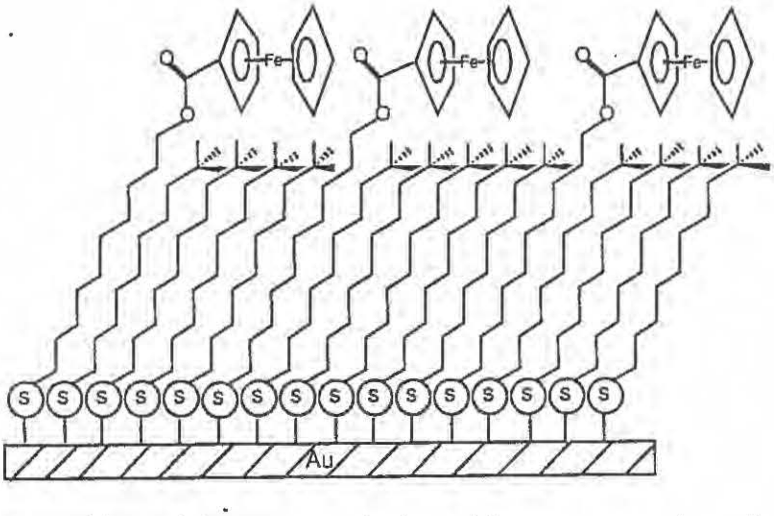
Interfacial electron transfer (et) plays a central role in many phenomena in chemistry and physics. The mechanism of et is exceedingly complex and events underlying it are often inaccessible to experimental investigations. For this reason, specialized systems are used to simplify interfacial et by minimizing the events that can occur [1]. One such system which has recently been utilized to understand interfacial et are functionalized self-assembled monolayers. Self-assembled monolayers have been studied in depth over the past decade revealing information concerning the structure, order, and stability of the systems [2]. A self-assembled monolayer that has been particularly well studied and characterized are the alkanethiol monolayers [3] which can be functionalized with redox-active molecules. Under proper assembly conditions a well-defined monolayer is formed which provides a spacer or interface between the redox-active molecule and the electrode that is easy to manipulate. Binding the electroactive moiety directly to the monolayer (as opposed to using a freely diffusing electroactive species) [4,5] has provided the bulk of insight in interfacial et.

When properly prepared these electroactive moieties bound to the monolayer exhibit ideal reversible behavior as shown by cyclic voltammetry. Usually, a small concentration or mole fraction of the redox-active molecule is incorporated into the monolayer by depositing it with a corresponding unsubstituted alkanethiol. Chidsey and co-workers have shown that when the mole fraction of the alkanethiol containing the bound redox-active molecule is small the monolayer exhibits non-adiabatic behavior and homogeneous electron transfer kinetics [6].



Monolayer with partial coverage of a bound ferrocene-terminated alkanethiol

Results of rate measurements performed on redox-active molecules bound to an alkanethiol monolayer strictly verify the prediction of the Marcus theory that there should be an exponential dependence on rate as the distance between the redox-active molecule and electrode is changed according to the following expression [7].

$$k^o_{app} = k^o \exp(-\beta d)$$

where k^o_{app} is the apparent rate constant, k^o is the rate constant at the bare electrode, β is the tunneling parameter, and d is the distance between the redox-active molecule and electrode. Li and Weaver [8] were the first to study this relationship utilizing an alkanethiol self-assembled monolayer. A linear plot of $\ln(k^o_{app})$ vs. distance (d) between the electroactive moiety and the surface (working electrode) has a linear slope and produces a β value of approximately 1 $Å^{-1}$ which is consistent with most systems studied by self-assembly techniques [8,9].

Strong electrolyte association with the redox-active molecule is observed as measured from the formation constant number [10] and from electrochemical quartz crystal microbalance measurements [11]. The strength of these interactions is shown to be dependent on the identity of the electrolyte.

By applying a slightly modified version of Nernst equation, double-layer effects influencing et rates can be explained. The modification is due to the electrostatic potential difference between the plane of electron transfer (PET) and the solvent [12]. This Nernst equation modification accounts for the observed increase of the redox potential when the concentration of the electrolyte is decreased, when the concentration of the redox-active molecule is increased, and when the electroactive moiety is located inside the alkyl chain.

By constructing Tafel plots it is shown that the Marcus treatment for et at electrodes fits to the experimental data well [13]. A plateau region is observed in these plots which arises as a direct consequence of a phenomenon analogous to the Marcus-inverted region [14]. The rate of et plateaus because no additional sites for et remain after a critical overpotential is reached.

References

1. Murray, R. W. *Molecular Design of Electrode Surfaces*; Interscience: New York, 1992.

2. (a) Nuzzo, R. G., Allara, D. L., "Adsorption of Bifunctional Organic Disulfides on Gold Surface," *J. Am. Chem. Soc.* **1983**, *105*, 4481.
   (b) Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D., "Spontaneously Organized Molecular Assemblies: 4. Structural Characterization of *n*-Alkyl Thiol Monolayers on Gold by Optical Ellipsometry, Infrared Spectroscopy, and Electrochemistry," *J. Am. Chem. Soc.* **1987**, *109*, 3559.

3. Dubois, L. H.; Nuzzo, R. G., "Synthesis, Structure, and Properties of Model Organic Surfaces," *Annu. Rev. Phys. Chem.* **1992**, *43*, 437.

4. Miller, C.; Grätzel, M., "Adsorbed ω-Hydroxy Thiol Monolayers on Gold Electrodes: Evidence for Electron Tunneling to Redox Species in Solution," *J. Phys. Chem.* **1991**, *95*, 877.

5. Chidsey, C. E. D., "Free Energy and Temperature Dependence of Electron Transfer at the Metal-Electrolyte Interface," *Science* **1991**, *251*, 919.

6. Chidsey, C. E. D.; Bertozzi, C. R.; Putvinski, T. M.; Mujsce, A. M., "Coadsorption of Ferrocene-Terminated and Unsubstituted Alkanethiols on Gold: Electroactive Self-Assembled Monolayers," *J. Am. Chem. Soc.* **1990**, *112*, 4301.

7. Marcus, R. A.; Sutin, N., "Electron Transfers in Chemistry and Biology," *Biochimica et Biophysica Acta* **1985**, *811*, 265.

8. Li, T. T.-T.; Weaver, M. J.; "Intramolecular Electron Transfer at Metal Surfaces. 4. Dependence of Tunneling Probability upon Donor-Acceptor Separation Distance," *J. Am. Chem. Soc.* **1984**, *106*, 6107.

9. (a) Finklea, H. O.; Hanshew, D. W., "Electron-Transfer Kinetics in Organized Thiol Monolayers with Attached Pentaammine(pyridine)ruthenium Redox Centers," *J. Am. Chem. Soc.* **1992**, *114*, 3173.
    (b) Becka, A. M.; Miller, C. J., "Electrochemistry at ω-Hydroxy Thiol Coated Electrodes. 3. Voltage Independence of the Electron Tunneling Barrier and Measurements of Redox Kinetics at Large Overpotentials," *J. Phys. Chem.* **1992**, *96*, 2657.
    (c) Chidsey, C. E. D., unpublished data.

10. Rowe, G. K.; Creager, S. E., "Redox and Ion-Pairing Thermodynamics in Self-Assembled Monolayers," *Langmuir* **1991**, *7*, 2307.

11. DeLong, H. C.; Donohue, J. J.; Buttry, D. A., "Ionic Interactions in Electroactive Self-Assembled Monolayers of Ferrocene Species," *Langmuir* **1991**, *7*, 2196.

12. Smith, C. P.; White, H. S., "Theory of the Interfacial Potential Distribution and Reversible Voltammetric Response of Electrodes Coated with Electroactive Molecular Films," *Anal. Chem.* **1992**, *64*, 2398.

13. Weber, K.; Creager, S. E., "Voltammetry of Redox-Active Groups Irreversibly Adsorbed onto Electrodes. Treatment Using the Marcus Relation Between Rate and Overpotential," *Anal. Chem.* **1992**, in press.

14. Marcus, R. A.; Siders, P., "Theory of Highly Exothermic Electron Transfer Reactions," . *Phys. Chem.* **1992**, *86*, 622.