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Evidence for Inefficient Chain-to-Chain Coupling in Electron Tunneling through Liquid Alkanethiol Monolayer Films on Mercury

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Distance dependence and the intervening medium effects continue to pin the attention of a large number of scientists as the key unresolved problems in the area of electron transfer kinetics.[1−3] In this communication, we report electrochemical results describing long-range electron transfer kinetics across two types of alkanethiol monolayer films of variable thickness. Our data show that the geometric distance decay constant involving a chain-to-chain tunneling pathway obtained for liquid monolayers is approximately 5 times smaller than the through-chain decay constant characteristic for ordered alkylthiol monolayers.

Many recent advances in the studies of intervening medium effects in electron tunneling have been made using the following two experimental approaches. In the first, synthetic donor/acceptor pairs are separated by rigid molecular spacer groups of controlled length and structure.[4−6] In the second, investigations involve redox proteins in which an electron acceptor (or donor) is attached to a specific site on the periphery of a protein.[3,7,8] In addition, electrochemical measurements in which molecules are tethered to the electrode surface at a specific distance have also been successfully explored.[9] In related research, recent studies of electron tunneling using self-assembled monolayers of alkanthiols as barrier films on gold electrodes have been particularly successful.[10−15] The experiments described below rely on alkanethiol monolayers assembled on mercury. The use of Hg electrodes allows us, for the first time, to vary the thickness of the monolayers in two different ways. The first involves the usual formation of ordered monolayers of thiols with alkyl chains of different length.[16] The second method is intrinsic only to Kublik type hanging mercury drop electrodes (HMDE).[17] Variation of the monolayer thickness is accomplished by careful expansion of the mercury drop using a micrometric screw that controls the volume of mercury extruded at the tip of the HMDE capillary.

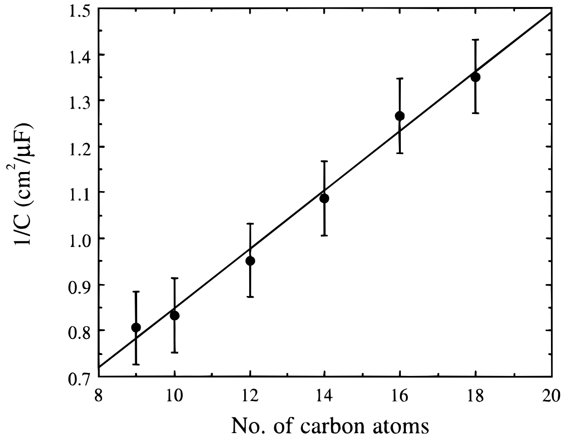

Figure 1. Reciprocal capacitance vs number of the carbon atoms in alkanethiols self-assembled on the HMDE. The differential capacitance was measured[25] in 0.5 M KCl solutions. The error bars are standard deviations of 10 measurements of different monolayers for each alkanethiol molecule.

Formation structure and properties of alkanethiol monolayers on gold are well documented in the literature.[18−21] Similar procedures lead to the formation of ordered thiol monolayers on mercury.[22,23] Indeed, our results suggest that impermeable monolayers of alkanethiols with chain length from 9 to 18 carbon atoms are formed essentially instantaneously on HMDE.[24] As shown in Figure 1, analysis of the differential capacitance (C) measurements[25] gave linear plots of $1/C$ vs number of the alkyl chain carbon atoms. This is consistent with the Helmholtz model of the double layer in which its capacitance is dominated by the hydrocarbon film of variable thickness (d)[12,26] and is expressed by

$$C = \epsilon\epsilon_o A/\mathrm{d} \qquad (1)$$

where A is the electrode surface area. The slope of these plots gave the dielectric constant of 2.2 ± 0.1, in agreement with the literature data.[12,16,18,19]

A typical cyclic voltammogram obtained at an HMDE coated with an alkanethiol monolayer in a 0.5 M KCl electrolyte containing 1.0×10^{-3} M $Ru(NH_3)_6^{3+}$ is shown in Figure 2 (curve A). It exhibits complete passivation of the electrode around the formal potential of the ruthenium probe ($E^{\circ\prime} = -0.197$ V) and an exponentially rising current at substantially more negative potentials. This is consistent with a kinetic limitation of current due to electron tunneling. In order to assess the distance dependence and to obtain the decay constant of electron tunneling, we plotted the logarithm of the tunneling current density (measured at -0.65 V vs SCE) vs the film

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† University of California at Berkeley.

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(1) Structure and Bonding: *Long Range Electron Transfer in Biology, 75*; Springer-Verlag: New York, 1991.

(2) Newton, M. D. *Chem. Rev.* **1991**, *91*, 767.

(3) Winkler, J. R.; Gray, H. B. *Chem. Rev.* **1992**, *92*, 369.

(4) Liang, N.; Miller, J. R.; Closs, G. L. *J. Am. Chem. Soc.* **1990**, *112*, 5353.

(5) Paulson, B.; Pramod, K.; Eaton, P.; Closs, G. L.; Miller, J. R. *J. Phys. Chem.* **1993**, *97*, 13042.

(6) Larson, S. L.; Hendrickson, S. M.; Ferrere, S.; Derr, D. L.; Elliott, C. M. *J. Am. Chem. Soc.* **1995**, *117*, 5881.

(7) Bjerrum, M. J.; Casimiro, D. R.; Chang I-J.; Billo Di, A. J.; Gray, H. B.; Hill, M. G.; Langen, R.; Mines, G. A.; Skov, L. K.; Winkler, J. R.; Wuttke, D. S. *J. Bioenerg. Biomembr.* **1995**, *27*, 295.

(8) Langen, R.; Chang, I-J.; Germanas, J. P.; Richards, J. H.; Winkler, J. R.; Gray, H. B. *Science* **1995**, *268*, 1733.

(9) Li, T. T-T.; Weaver, M. J. *J. Am. Chem. Soc.* **1984**, *106*, 6107.

(10) Chidsey, C. E. D. *Science* **1991**, *251*, 919.

(11) Finklea, H. O.; Hanshew, D. D. *J. Am. Chem. Soc.* **1992**, *114*, 3173.

(12) Miller, C.; Cuendet, P.; Gratzel, M. *J. Phys. Chem.* **1991**, *95*, 877.

(13) Miller, C.; Gratzel, M. *J. Phys. Chem.* **1991**, *95*, 5225.

(14) Becka, A. M.; Miller, C. J. *J. Phys. Chem.* **1992**, *96*, 2657.

(15) Cheng, J.; Saghi-Szabo, G.; Tossell, J. A.; Miller, C. J. *J. Am. Chem. Soc.* **1996**, *118*, 680.

(16) Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1987**, *109*, 3559.

(17) Kemula, W.; Kublik, Z. *Anal. Chim. Acta* **1958**, *18*, 104.

(18) Dubois, L. H.; Nuzzo, R. G. *Ann. Rev. Phys. Chem.* **1992**, *43*, 437.

(19) Ulman, A. *An Introduction to Ultrathin Organic Films; From Langmuir-Blodgett to Self Assembly*; Academic Press: San Diego, CA, 1991.

(20) Bard, A. J.; Abruna, H. D.; Chidsey, C. D.; Faulkner, L. R.; Feldberg, S. W.; Itaya, K.; Majda, M.; Melroy, O.; Murray, R. W.; Porter, M. D.; Soriaga, M. P.; White, H. S. *J. Phys. Chem.* **1993**, *97*, 7147.

(21) Laibinis, P. E.; Bain, C. D.; Nuzzo, R. G.; Whitesides, G. M. *J. Phys. Chem.* **1995**, *99*, 7663.

(22) Demoz, A.; Harrison, D. J. *Langmuir* **1993**, *9*, 1046.

(23) Bruckner-Lea, C.; Kimmel, R. J.; Janata, J.; Conroy, J. F. T.; Caldwell, K. *Electrochim. Acta* **1995**, *40*, 2897.

(24) The monolayers were self-assembled from 20% hexadecane solutions. HMDE was rinsed with ethanol and transferred to a 0.5 M KCl solution. We observed no systematic differences in the results of the subsequent capacitance measurements regardless of the duration of the self-assembly step in the range from 5 s to 10 min.

(25) The differential capacitance of the alkanethiol-coated electrodes was measured by a fast scan ($v = 1.0$ V/s) cyclic voltammetry between -0.1 and -0.6 V vs SCE. Flat charging current (i_c) traces were obtained and analyzed according to $i_c = vC$. Polarization of monolayer-coated HMDE's beyond -0.9 V vs SCE results in their desorption.

(26) The film thickness was calculated using the known bond lengths and angles. In addition, 1.0 Å was taken as a van der Waals radius of the terminal methyl groups. An all-trans conformation and the perpendicular orientation of the alkyl chains with respect to the electrode surface were assumed.

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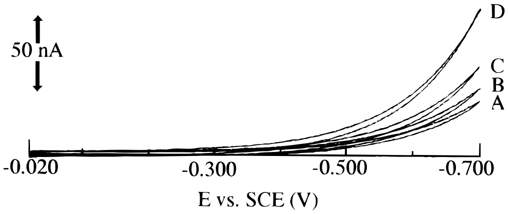

Figure 2. Cyclic voltammograms recorded in a 1.0 × 10^{-3} M $Ru(NH_3)_6^{3+}$, 0.5 M KCl solution at a Hg drop electrode coated with a dodecanethiol monolayer before and in the course of the HMDE expansion; $\upsilon = 50$ mV/s. A: before expansion, $A = 0.0230$ cm^2. B: $A = 0.0246$ cm^2. C: $A = 0.0258$ cm^2. D: $A = 0.0274$ cm^2.

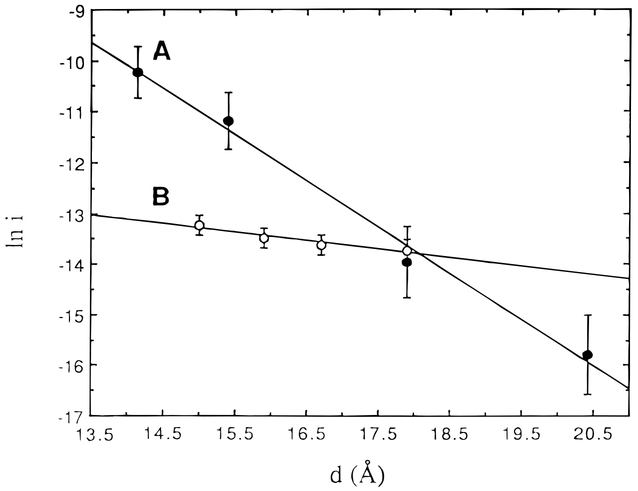

Figure 3. Plots of the tunneling current density vs. film thickness at −0.65 V vs SCE measured in 1.0 × 10^{-3} M $Ru(NH_3)_6^{3+}$, 0.5 M KCl solutions at the HMDE coated with alkanethiol monolayers. A: Electrodes were coated with ordered nonanethiol, decanethiol, dodecanethiol, and tetradecanethiol monolayers.[27] The error bars represent standard deviations of 10 measurements of different monolayers. The film thickness was calculated on the basis of the known molecular structure of the alkanethiols.[26] B: Electrodes were coated with the dodecanethiol monolayers and expanded. The data represent the average and standard deviations of four independent series of experiments including that in Figure 2; $\beta' = 0.16 \pm 0.08$ Å^{-1}.

thickness[26] for a number of alkanethiols (see Figure 3). The slope gave the decay constant $\beta = 1.2 \pm 0.1$ per carbon atom or 0.96 ± 0.08 Å^{-1}.[27] When ferricyanide replaced $Ru(NH_3)_6^{3+}$ in the same types of experiments, we obtained an identical β value. These values agree well with the literature data for the electrochemical tunneling experiments involving alkanethiol films on gold.[12,14] We note that this agreement as well as the agreement of the dielectric constant with the literature data reported above substantiates our assumption of the perpendicular orientation of alkanethiols with respect to the mercury surface. This orientation, as opposed to the 30° tilt of the chains found on gold(111),[18] is reasonable in view of an expected nonepitaxial self-assembly of alkanethiols on the liquid mercury substrates.

The mercury drop expansion experiments were carried out in an aqueous electrolyte solution following self-assembly of alkanethiols with 10, 12, or 14 carbon atom chains.[28] In all cases, slow expansion of an HMDE resulting in as much as 20% increase of its surface area maintained the initial passivating character of the monolayer, but resulted in an increase of the tunneling current as shown in Figure 2 (curves B, C, and D). This suggests that the alkanethiol monolayers become liquid or tilted upon electrode expansion and that their continuous pinhole-free character is preserved. To confirm this hypothesis, we analyzed the relationship between the charging current (i_c) and the electrode surface area. This relationship can be easily predicted when one realizes that the decrease of the film thickness should be inversely proportional to the increase of the electrode surface area. In other words, we expect the film volume (V_f) to be constant throughout the expansion experiment: $Ad = V_f =$ const.[29] Combining this with $i_c = \upsilon C$ and eq 1 gives

$$i_c = \upsilon\epsilon\epsilon_o A^2/V_f \qquad (2)$$

As expected, we obtained linear i_c vs A^2 plots ($r > 0.99$). Their slopes yielded $\epsilon = 2.2 \pm 0.2$ (for 10 series of experiments involving C_{10}, C_{12}, and C_{14} thiols); the same value as reported above. HMDE expansions beyond 20% of the initial surface area, as well as attempts to expand longer or shorter chain alkanethiol monolayers, resulted in large diffusion-limited faradaic currents, reflecting formation of discontinuous monolayers. Similar drop expansion experiments involving mercury electrodes coated with octanethiol and octadecanethiol have been recently reported by Bruckner-Lea and co-workers.[23] Consistently with our observations, expansion of those monolayers also yielded discontinuous films and resulted in large diffusion-controlled faradaic current.

Analysis of the tunneling current density observed in the HMDE expansion experiments (such as those in Figure 2) in terms of ln *i* vs *d* (see Figure 3) gave linear plots with $\beta' = 0.2 \pm 0.1$ Å^{-1} (the average and SD of 10 series of experiments with C_{10}, C_{12}, and C_{14} thiols). This distance decay constant is 5 times smaller than β obtained in the first series of experiments. Both plots involved geometric distance of electron tunneling and thus yielded substantially different intercepts. Thus, as can be seen in Figure 3, decrease of the film thickness in the HMDE expansion experiments results in a much smaller increase of the tunneling current than that observed in the experiments in which the film thickness was varied by self-assembly of thiols with decreasing chain length.

To analyze these measurements, we note first that the tunneling current density involving a through-chain pathway should be largely invariant in the drop expansion experiments, since the distance along this pathway does not change as an HMDE is expanded. In fact, since monolayer expansion may introduce gauche and other conformations, a small decrease of the electron-tunneling efficiency might be expected[2] that would result in a negative β'. Therefore, the observed small *increase* of current density must correspond to a new, albeit less efficient, tunneling pathway. We believe that this pathway must involve chain-to-chain coupling. The large difference between β and β' values is the first direct evidence that the chain-to-chain coupling pathway is significantly less efficient than the through-chain path in electron tunneling across alkanethiol monolayers. This conclusion is consistent with the assessment of the coupling efficiency of the through-space vs through-bond tunneling pathways in proteins.[30,31]

Ability to form liquid alkanethiol monolayers of continuously variable thickness demonstrated in this report opens a possibility to investigate electron tunneling through other single- or two-component type liquid monolayer systems, a possibility which promises new data concerning the role of the intervening medium in electron tunneling kinetics.

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(27) In the experiments with $Ru(NH_3)_6^{3+}$, an electron tunneling current observed at electrodes coated with hexadecanethiol and octadecanethiol monolayers was too small to be measured reliably.

(28) The initial surface area of HMDE was 0.0230 ± 0.0002 cm^2 (the average and SD of 20 determinations made by weighing 10 drops of mercury). The drop expansion experiments were carried out in small increments each increasing the electrode surface area by ca. 7% of its initial value.

(29) This is a good approximation in view of a negligible difference between the densities of liquid and solid hydrocarbons. For example, at 20 °C the density of liquid hexadecane is less than 0.5% smaller than the density of solid octadecane at the same temperature (0.7768 vs 0.7733 g cm^{-3}).

(30) Wuttke, D. S.; Bjerrum, M. J.; Winkler, J. R.; Gray, H. B. *Science* **1992**, *256*, 1007.

(31) Curry, W. B.; Grabe, M. D.; Kurnikov, I. V.; Skourtis, S. S.; Beratan, D. N.; Regan, J. J.; Aquino, A. J. A.; Beroza, P.; Onuchic, J. N. *J. Bioenerg. Biomembr.* **1995**, *27*, 285.