

Evaluation of the Tunneling Constant for Long Range Electron Transfer in Azobenzene Self-Assembled Monolayers on Gold

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Introduction

The electron transfer at interfaces is of primary importance in chemical, biological, and other natural processes, which has led to scientists making continuous efforts to pursue ideal models to study the basic issues for the electron transfer processes.¹ After Nuzzo and Allara reported the formation of highly organized monolayers based on the Au-sulfur interaction,² the creation of well-defined self-assembled monolayers (SAMs) has provided an ideal model in the study of interfacial electrochemistry. It presents us with a unique opportunity to investigate the fundamental issues such as the distance dependence and the effect of interfacial structure on the long range electron transfer.³⁻¹⁷ Miller and Becka⁵ have systematically explored the use of an inert self-assembled monolayer on gold as a blocking layer toward dissolved redox molecules. From the dependence of the electron transfer rate of a series of redox couples on the thickness of the monolayer film, the tunneling constant in the hydroxyl thiol was measured independent of the redox couple,⁵ while Li⁶ reported the value in the long-chain alkanethiol monolayers. In the meantime, Chidsey⁷⁻⁹ and Finklea¹⁰⁻¹⁴ have constructed reversible redox center (ferrocene or pentaammine (pyridine) ruthenium) tethered self-assembled monolayers on gold and investigated their electron-transfer kinetics in detail. Recently, the investigation on the distance dependence of electron transfer in electroactive self-assembled monolayers has been extended to viologen,¹⁵ quinone,¹⁶ and a ferrocene LB-SAM composite bilayer.¹⁷ The electron tunneling constant of respective system was addressed experimentally.

However, up to date, no experimental data have yet been provided concerning the tunneling constant for long range electron transfer in SAMs with attached complex redox centers such as azobenzene, which possesses pro-

Scheme 1

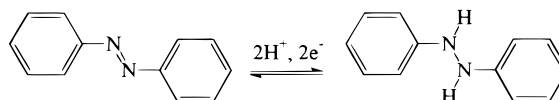
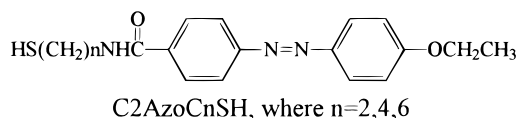


Chart 1



tonation reaction and structural change. In this note, we will describe our results about the evaluation of the electron tunneling constant for electron transfer of azobenzene self-assembled monolayers on gold. The novelty of this work is on the functional group azobenzene. It has a multistep reduction/oxidation behavior during which the molecular structure definitely changes (Scheme 1). It might be of great interest to compare the results of azobenzene SAMs with those simple redox center derived SAMs. Further, together with the previous studies on the azobenzene SAMs (as examples, see refs 18-21), the present investigation does help us to gain deep insights into the electrochemical reaction nature of azobenzene organized molecular assemblies.

Experimental Section

To serve the intended task of investigating the alkyl chain spacer dependent electron transfer kinetics in azobenzene SAMs, we have prepared a set of azobenzenealkane thiols with different spacer chain lengths (Chart 1), which were abbreviated as C2AzoCnSH ($n = 2, 4, 6$) in the following descriptions. The detailed procedure for the preparation and purification of these molecules was reported before.¹⁸

The gold substrate was obtained by vacuum evaporation of high-purity gold (99.99%) onto a clean surface of glass, which had been precoated with chromium to improve adhesion. The C2AzoCnSH SAMs were formed by immersing "piranha solution" cleaned gold substrates into 1.0 mM C2AzoCnSH/C₂H₅OH solution for about 24 h. After immersion, the sample was washed sequentially with ethanol and distilled water.

Electrochemical characterization was carried out in a single-compartment, three-electrode, glass cell containing an Ag|AgCl|satd KCl reference electrode and a Pt wire counter electrode. Voltammetric measurements were made on a Hokuto Denko HA-150 potentiostat combining with a Hokuto Denko HB-III function generator, and the voltammetric signals were recorded on a Riken Denshi F-35A X-Y recorder. All experiments were carried out at ambient laboratory temperature ($20 \pm 2^\circ\text{C}$) in solution free from oxygen by bubbling with nitrogen.

Results and Discussion

The formation of monolayers on a gold surface is in a spontaneous and reproducible manner with all of the azobenzenealkane thiol molecules C2AzoCnSH ($n = 2, 4, 6$) we have prepared. Figure 1 shows the typical cyclic voltammograms of C2AzoCnSH ($n = 2, 4, 6$) SAM modified gold electrodes. They were measured in a Britton-Robinson (B-R) buffer at pH 5.2 with a sweep rate of 100 mV/s. In each voltammogram, a single peak wave of redox

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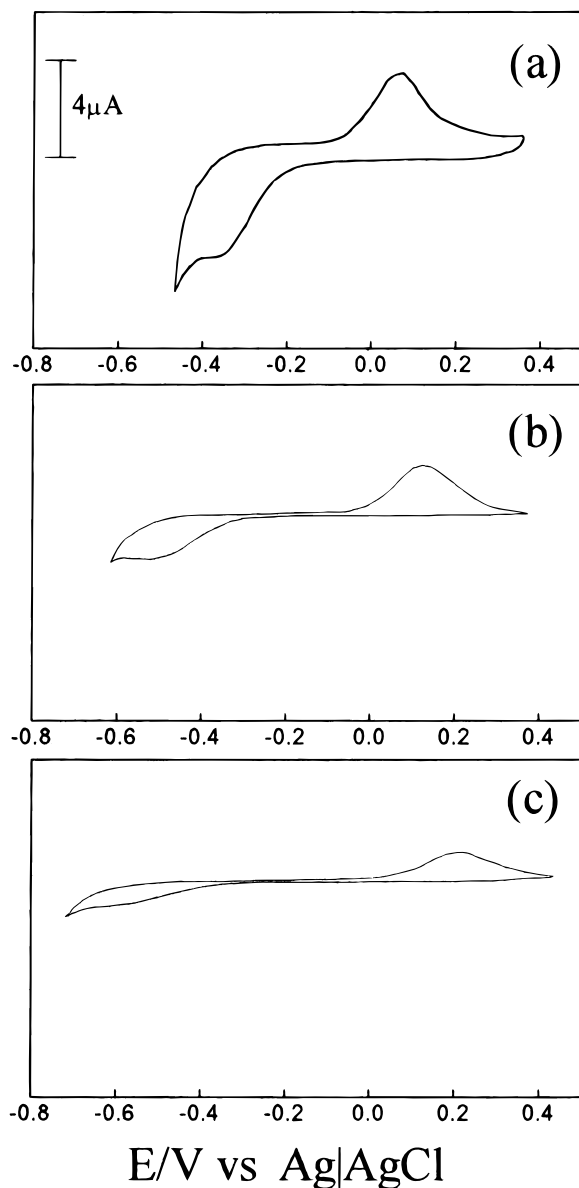


Figure 1. Cyclic voltammograms of C2AzoCnSH/Au SAMs (a–c for $n = 2, 4$, and 6 , respectively) in Britton–Robinson buffer, pH 5.2, 0.1 M NaClO₄. Scan rate was 0.1 V/s. Electrode area was 0.36 cm².

couple due to the reduction/oxidation of the azobenzene moiety in the monolayer was observed (Scheme 1).^{18,19} However, the shape of the voltammetric waves deviated from the predicted one for an immobilized redox couple. The remarkably large separation between anodic peak and cathodic peak ($E = E_{p,a} - E_{p,c}$) was found for all of these azobenzene monolayers. On the other hand, the E value increased with the potential scan rate, indicating that the electrode reaction might be controlled by electron transfer kinetics when we take into account of the factor that the protonation reactions are kinetically in equilibrium.¹⁸ As the alkyl chain spacer becomes longer, redox peak splitting E at the same potential scan rate became larger as shown in Figure 1, suggesting that there is a decrease in electron transfer rate with the alkyl chain spacer thickness increasing (see following section).

The surface concentration (Γ_{azo}) of electroactive azobenzene groups was estimated by the integration of the current associated with the azobenzene redox waves, taking a two-electron, two-proton reaction mechanism (Scheme 1). The Γ_{azo} values for C2AzoCnSH ($n = 2, 4, 6$) SAMs on gold are listed in Table 1 for comparison. There is a distinct

Table 1. Surface Concentration of Electroactive Azobenzene Group and Double Layer Capacitance Data of C2AzoCnSH/Au SAMs

n	$\Gamma_{\text{azo}}/(10^{-10} \text{ mol/cm}^2)$	$C/(\mu\text{F/cm}^2)$
Au		54.6
2	4.21	11.0
4	2.51	2.7
6	1.34	1.4

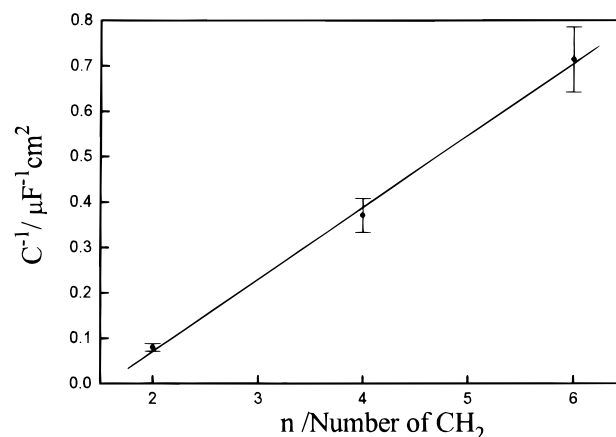


Figure 2. Reciprocal of capacitance (C^{-1}) at -0.2 V (vs Ag|AgCl|satd KCl) vs n for C2AzoCnSH SAMs.

decrease in the amount of electroactive azobenzenes in the monolayer with the spacer chain length increasing. That is to say, the longer the alkyl spacer chain length, the smaller the amount of azobenzene groups electro-accessible in the SAMs on gold, in accord with the phenomenon observed by Mirkin in long chain azobenzene SAMs.^{20,21} However, this is different from what we have previously studied using azobenzene SAMs with different terminal chain length (CnAzoC2SH, $n = 1, 2, 3$).¹⁹ In that case, when the terminal group consists of less than four methylenes, the surface concentration of azobenzene moieties becomes higher when the n value increases, excluding the possibility of inactive azobenzene within CnAzoC2SH ($n = 1, 2, 3$) SAMs. The different electrochemical accessibility of azobenzene SAMs has been further investigated by electrochemical in situ FTIR studies recently.^{22,23}

Another means to examine the packing structure of a monolayer on the electrode surface is the measurement of interfacial capacitance. The differential capacitance data for azobenzene SAMs were calculated from the capacitive current at -0.2 V (vs Ag|AgCl) and are also listed in Table 1. It should be pointed out that there is a deviation within 10% for these data. Obviously, the modification of gold electrode with an azobenzene monolayer caused a dramatic decrease in the electrode/electrolyte capacitance. On the other hand, the capacitance value for C2AzoCnSH SAM modified electrode decreases significantly with an increase of the spacer chain length. Figure 2 represents the reciprocal of the differential capacitance, C^{-1} , as a function of the length of spacer alkyl chain. The solid line is a linear regression analysis C^{-1} for $n = 2-6$, which shows that the differential capacitance for C2AzoCnSH SAMs is inversely proportional to the length of the spacer alkyl chain. The slope of this line is 0.15 cm²/μF per CH₂ group, considerably larger than the value (0.055 cm²/μF) for n -alkanethiol

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Table 2. Electrochemical Kinetic Parameters of C2AzoCnSH/Au SAMs

<i>n</i>	<i>E</i> ^o /V (vs Ag AgCl)	αn	$(1 - \alpha)n$	$\ln k_{\text{app}}/\text{s}^{-1}$
2	-0.15	0.91	0.93	-11.1
4	-0.20	1.00	0.97	-14.5
6	-0.22	1.05	1.05	-16.5

monolayers (CnSH, *n* > 9) reported by Porter et al.²⁴ The Helmholtz theory can be used to model the double layer as an ideal capacitor for which the reciprocal of the capacitance (per area) is,

$$C^{-1} = d/\epsilon\epsilon_0 \quad (1)$$

where *d* is the thickness of the dielectric medium that separates the two conducting plates, ϵ is the dielectric constant of the separation medium, and ϵ_0 is the permittivity of free space. On the basis of this model, an increase of C^{-1} (or the decrease of *C*) corresponds to an increase of *d* (the film thickness) or the change of dielectric constant. As a comparative system, we have shown that with longer terminal group in azobenzene SAMs, the packing density has been improved accordingly.¹⁹ In general, a very ordered and closely packed monolayer is expected with an adsorbate molecule having a longer alkyl chain.^{18,25}

To gain deep insights into the distance dependence of the electron transfer of azobenzene in SAMs, we further performed a kinetic treatment of this system. From those redox splittings larger than 200 mV/*n*, the electron transfer rate constant can be extracted from the eqs 2 and 3 derived for the totally irreversible surface electrochemical reactions by Laviron²⁶

$$E_{\text{p,c}} - E^{\circ} = (RT/\alpha nF) \ln(\alpha nFv/FTk_{\text{app}}) \quad (2)$$

$$E_{\text{p,a}} - E^{\circ} = [RT/((1 - \alpha)nF)] \ln[(1 - \alpha)nFv/RTk_{\text{app}}] \quad (3)$$

where the notation *v* means the potential scan rate and *R*, *T*, and *F* have their usual meanings. Assuming that the product *n* does not vary with potential, the plots of $E_{\text{p,c}} - \ln(v)$ and $E_{\text{p,a}} - \ln(v)$ have been fitted with linear regression. The respective slopes of the lines are $RT/(\alpha nF)$ and $RT/((1 - \alpha)nF)$. The values of *n* and $(1 - \alpha)n$ were thus obtained and substituted back in eqs 2 and 3 to solve for k_{app} .

Table 2 gives the corresponding kinetic parameters for C2AzoCnSH (*n* = 2, 4, 6) SAMs on gold. The apparent electron transfer rate constants of the present system are all under the order of 10^{-4} s^{-1} , considerably smaller than those in LB films²⁷ and the simple adsorption case.²⁸ Further, the dependence of logarithmic rate constants on the number of carbon atoms in the spacer chain shows a significant decrease, which could be fitted with a linear regression (Figure 3). We noted from Table 2 that the thermodynamic indicator, i.e., the formal potential in these azobenzene SAMs, slightly changes with various alkyl spacer chain lengths, indicating there are some thermodynamic changes in the environment around the redox center. It may reflect the influence of the molecular order in the monolayer on the redox behavior of azobenzene.

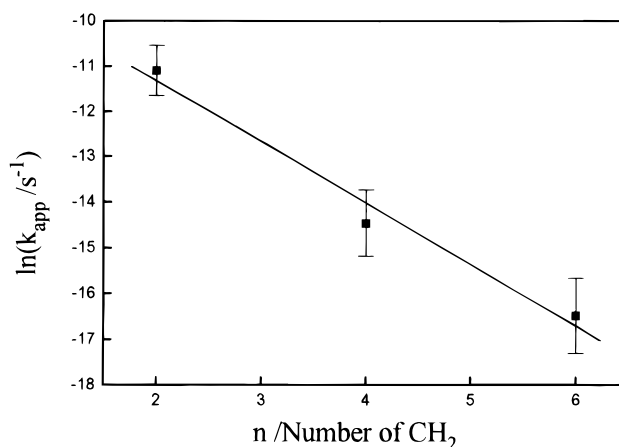
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**Figure 3.** Dependence of $\ln k_{\text{app}}$ on the number of CH₂ involved in the alkyl chain spacer of C2AzoCnSH/Au SAMs.**Table 3. Electron Tunneling Constants Derived from Different SAM Systems**

system	β value	reference
Co ^{III} (NH ₃) ₅ X-SAM	1.45 Å ⁻¹	Weaver ³
Fe(CN) ₆ ^{3-/4-} /SAM	0.90/CH ₂	Miller ⁴
Fe(CN) ₆ ^{3-/4-} /SAM	(1.08 ± 0.2)/CH ₂	Miller ⁵
Fe(CN) ₆ ^{3-/4-} /SAM	(1.02 ± 0.2)/CH ₂	Li ⁶
Ru-derived SAM	(1.06 ± 0.04)/CH ₂	Finklea ¹⁰
viologen SAM	0.006 Å ⁻¹	Willner ¹⁵
Fc-SAM	(1.21 ± 0.05)/CH ₂	Chidsey ⁹
Fc-LB/SAM	0.96/CH ₂	Mclendon ¹⁷
quinone-SAM	0.42/CH ₂	Takehara ¹⁶
azo SAM	(1.34 ± 0.2)/CH ₂	this work
semiempirical model	0.76/CH ₂	Hopfield ³⁷
ab initio calculation	~0.5–0.9 Å ⁻¹	Newton ³⁸

On the basis of the electron tunneling mechanism, the distance dependence of the electron transfer rate is given by the Marcus theory²⁹ in eq 4

$$k_{\text{et}} \propto \exp[-\beta(d - 3)] \exp[-(\Delta G^{\circ} + \lambda)^2/4RT\lambda] \quad (4)$$

where *d* is the distance between the redox center and the electrode surface, ΔG° and λ are the free energy change and reorganization energy associated with the electron transfer, while β is the electron tunneling constant. Supposing that the free energy and reorganization energy for all of the azobenzene monolayer systems are similar, then the electron transfer rate constant should exponentially depend on the alkyl chain spacer length and can be expressed by³

$$k = k_0 \exp[-\beta(r - r_0)] \quad (5)$$

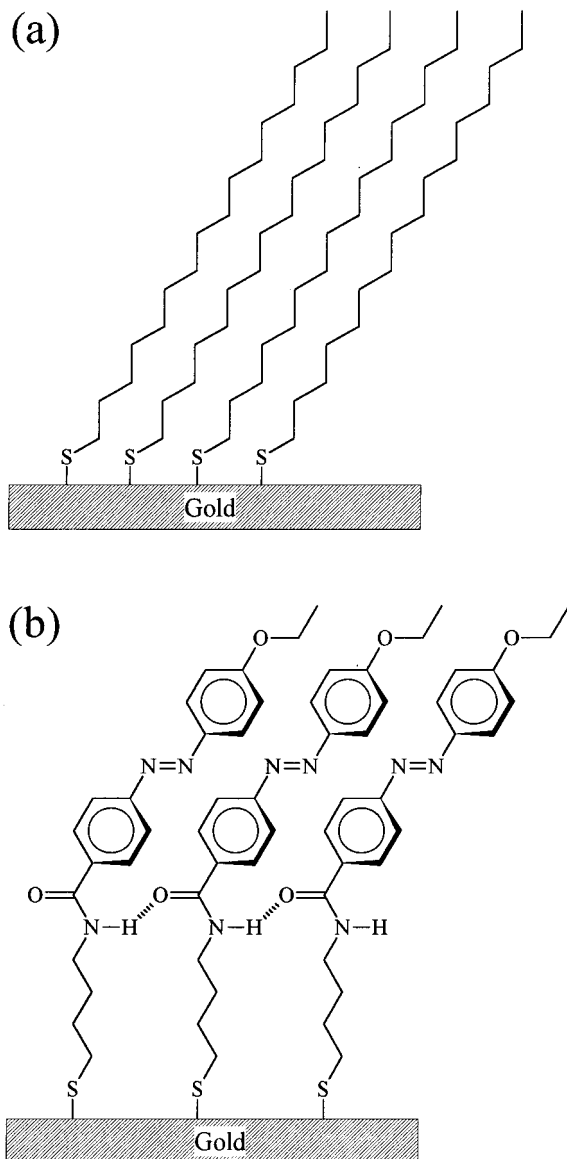
The value of the tunneling parameter β can be obtained from the slope of the $\ln k_{\text{app}} \sim n$ plot as shown in Figure 3. The tunneling coefficient in the present system was determined to be 1.34 ± 0.2 per methylene group.

In retrospect, there are several reports about the evaluation of the tunneling parameter for electron transfer within a set of self-assembled monolayers.^{3–6,9,10,14–17} We added our result into the list (Table 3), by which we can describe the difference among these systems more clearly.

The experimental value of $\beta = (1.34 \pm 0.2)/\text{CH}_2$ (Figure 3) for our azobenzene system is a little larger than the value of $\beta = (1.06 \pm 0.04)/\text{CH}_2$ measured by Finklea for PyRu(NH₃)₅ moieties with alkanethiol tethers and matching length dilute alkanethiols,¹⁰ the value of $\beta = (1.21 \pm 0.05)/\text{CH}_2$ for the ferrocene system obtained by Chidsey⁸

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Chart 2



and the values of β measured for self-assembled thiol films (on gold electrodes) with redox moieties in solution: $(1.08 \pm 0.2)/\text{CH}_2$ for aqueous $\text{Fe}(\text{CN})_6^{3-/4-}$, $\text{Ru}(\text{NH}_3)_6^{3+/2+}$, and $\text{Fe}^{3+/2+}$ with ω -hydroxythiol films ($n = 6-22$);⁵ and $(1.02 \pm 0.2)/\text{CH}_2$ for aqueous $\text{Fe}(\text{CN})_6^{3-/4-}$ and $\text{Fe}^{3+/2+}$ with alkanethiol films ($n = 12-18$).⁶ Nevertheless, it should be careful to convert the β value into a distance unit, because we require a clear description about the orientation and conformation of the monolayer. The IR spectroscopic, X-ray photoelectron spectroscopy (XPS), and ellipsometric data indicate that the long-chain thiols or terminal-substituted long-chain thiols $\text{X}(\text{CH}_2)_{15}\text{SH}$ ($\text{X} = \text{CH}_3$, CH_2OH , CO_2H , CO_2CH_3 , and CONH_2) form a densely packed, crystalline-like assembly with fully extended alkyl chains tilted from the surface normal by an angle of about $\sim 30^\circ$.^{18,30} The model calculation has also given out the same description of the molecular orientation of these monolayers on gold surface³¹ (see Chart 2a). But it is quite different in the molecular orientation of monolayers derived from amidethiol, which has been shown to be nearly perpendicular to the surface with interchain

hydrogen bond networks³²⁻³⁵ (see Chart 2b). If we take the C–C bond length as 1.54 \AA ,³⁶ with the addition of one methylene group the increase of film thickness should have values 1.10 and 1.27 \AA for the two different molecular orientation models, respectively. On the basis of above considerations, the corresponding value of the $\beta = 1.06 \text{ \AA}^{-1}$ in the present azobenzene system lies within the upper range of the experimentally addressed values from reversible redox center tethered monolayer systems^{8,10} and alkanethiol monolayers with redox centers in solution.^{5,6} Further, it is also larger than the theoretical value ($\sim 0.5-0.9 \text{ \AA}^{-1}$),^{37,38} but smaller than the estimated β ($1.3-1.8 \text{ \AA}^{-1}$) for the classical through-space tunneling.^{10,39,40}

The evaluation of the exact meaning of such a β value is not in hand at present, but we believe that besides the distance effect for electron transfer, it should be correlated with the electrochemical reaction nature of azobenzene due to its structural change and protonation related redox process. When the hydrazobenzene is formed upon the reduction of the monolayer, conformational changes associated with the conversion of the planar azobenzene group⁴¹ into the kinked hydrazobenzene form⁴² must be inhibited by the rigid film structure, as well as the blocking effect of the ion transportation into the monolayers (see Scheme 1). All these effects are of unambiguous importance to evaluate the apparent electron-transfer kinetic rate constants of azobenzene SAMs. We have shown that in azobenzene SAMs with different terminal groups (CnAzoC_2SH , $n = 1, 2, 3$) (in which the electron transfer distance is identical), the apparent electron transfer rate constant decreases with terminal group chain length increasing.¹⁹ In that case, the spatial inhibition in redox process of azobenzene was considered to contribute to the decrease of the apparent electron transfer rates. The similar effect from the increasing of molecular packing density should also hold true when the spacer alkyl chain length increases from $n = 2$ to 6. Thus the decrease of apparent electron transfer rate constant may derive from both the distance dependence and the molecular packing changes. Due to limitation of the method we used to obtain the value, it is expected that the real value of β in $\text{C}_2\text{AzoC}_n\text{SH}$ ($n = 2-6$) might be smaller than our present experimentally addressed one. For a comparative system, naphthoquinone anchored SAM, which also undergoes a two-electron, two-proton redox process but without changes in molecular conformation, we noted that Takehara et al. have reported a much smaller β value (0.36 \AA^{-1}).¹⁶ However, the structure of their system is not well-defined because of the limitation in their preparing procedure and molecular structure.

The calculation of the barrier height may help us to further give insights into the contribution from the increased structural inhibition in the process of electron transfer in our azobenzene SAMs. Principally, if we assume a rectangular barrier,⁴³ β gives a measure of the

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barrier height through the formula:

$$\beta = 4\pi(2m)^{1/2} V^{1/2}/h \quad (6)$$

where m is the free electron mass, h is the Planck constant, and V is the height of the barrier in electron volts. Substituting the values of the constants in eq 6, we can obtain

$$\beta = 1.025 V^{1/2} \quad (7)$$

A β value of 1.06 \AA^{-1} corresponds to a barrier height of 1.07 eV. The value is considerably larger than the previously determined barrier height of *ca.* 0.4–0.7 eV,^{6,44,45} which may also reflect the contribution from the increasing of structural inhibition in addition to the distance effect.

In summary, we presented here the evaluation of the electron tunneling parameter for the azobenzene self-assembled monolayers on a gold electrode surface by cyclic voltammetry. The experimental value of $\beta = (1.34 \pm 0.2)/$

CH_2 for our azobenzene system lies within the upper range of the values for reversible redox centers in solutions or tethered monolayer systems^{5,6,9,10} and those obtained from the model calculations.^{37,38} Further, it is smaller than the value estimated for classical through space tunneling.^{10,39,40} The exact electron tunneling mechanism in this system is not clear, which needs further information from other comparative experiments such as chronoamperometry and ac impedance. Nevertheless, we emphasize that our result indicated that the distance dependent electron transfer kinetic behavior in azobenzene monolayer systems might be associated with the spatial hindrance of the monolayer structure on the redox process from azobenzene to hydrazobenzene. The present investigation and the comparison with previous studies suggest that the molecular packing nature plays an important role in long range electron transfer in organized monolayer assemblies, thus proving the importance in evaluation of relationship between the structural nature and the functionality in these model systems.

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