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A simple comparison of interfacial electron-transfer rates for surface-attached and bulk solution-dissolved redox moieties

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Abstract

A relationship is developed that facilitates a comparison between the standard electron-transfer rate constant (k^0) of a redox couple covalently attached (as a constituent of a self-assembled monolayer (SAM)) to an electrode and the k^0 of a similar redox couple dissolved in an electrolyte solution in contact with a similar (but not electroactive) electrode/SAM assembly. Such comparisons performed for ferrocene and ruthenium redox couples demonstrate that the (normalized) rate of electron-transfer (and, also, the electronic coupling) for a solution-dissolved couple through an alkanethiol SAM/aqueous electrolyte solution interface is, within one order of magnitude, equal to that for a covalently attached redox species. A related comparison involving the Marcus theory limiting rate constants for solution-dissolved couples and the Arrhenius preexponential factors for attached couples supplies additional evidence for this surprising result.

Keywords: Interfacial electron-transfer kinetics; Electron tunneling; Surface-attached redox couples; Solution-dissolved redox couples

1. Introduction

Measurements of the kinetics of interfacial electron-transfer (ET) reactions are currently of great scientific and technological interest [1,2]. In regard to these interests, for example, we have discussed a method that employs such measurements on redox couples tethered to electrodes via intervening self-assembled monolayer (SAM) films to estimate the electrical resistance of the resulting junctions [3,4]. These SAMs are comprised of oligomeric chains, and those which covalently link the redox couples to the electrodes are denoted below as bridges. Such measurements are relevant to the emerging field of molecular electronics [5].

For nonadiabatic electron-transfer reactions, the chemical composition and length of the bridge between the redox couple and the electrode (or the chemical composition and thickness of the intervening medium between the redox couple and the electrode for a solution-dissolved redox couple) are of critical importance in determining the electronic coupling between the couple and the electrode and the rate of the ET reaction [3,4,6]. Also of critical importance for the electronic coupling is the nature of the contact (either covalent or electrostatic or van der Waals) between the redox couple and the remainder of the electron transfer system [3,4,7]. It is, therefore, of interest to compare the rates of electron-transfer of redox couples covalently attached to metallic electrodes as constituents of the electrode-bridge-redox couple structures described above [8] with those of chemically similar redox couples dissolved in electrolyte solutions in contact with electrodes coated with insulating films (i.e., non-electroactive SAMs [1]). These comparisons are also of consequence because studies of the interfacial ET kinetics of redox couples in solution at monolayer coated electrodes are not subject to the complicating factors caused by redox couple adsorption on bare electrodes [9].

This paper presents and discusses such comparisons for alkanethiolate SAMs based on measurements of the interfacial ET kinetics of ferrocene and ruthenium (e.g., $Ru(NH_3)_6^{3+/2+}$) redox moieties accomplished by a number of groups including ours. Section 2 describes the theory and calculations that facilitate these comparisons. Section

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3 presents the comparisons and discusses the intriguing conclusion derived from these comparisons that the interfacial electron-transfer rate for these particular redox moieties does not depend significantly upon whether or not the redox moiety is covalently linked to the electrode. Some implications of this conclusion are discussed in Section 4.

2. Theory

For a redox moiety attached to an electrode by a bridge of length ℓ_A which is a constituent of a mixed SAM comprised of electrode-bridge-redox couple structures and diluent (non-electroactive) alkanethiolates, the standard ET rate constant ($k_A^0(\ell_A)$; units: s^{-1}) is defined by [10,11]

$$k_A^0(\ell_A) = k_A^0(0)\exp(-\beta_B\ell_A) \tag{1}$$

where β_B is the exponential decay coefficient associated with the bridge and $k_A^0(0)$ includes the effect of the covalent connection on the electronic coupling. Eq. (1) signifies that the ET reaction is effected by electrons tunneling through the bridge (i.e., the electron-transfer is assumed to be non-adiabatic) and that the electrons do not tunnel through the diluent component of the mixed SAM [4]. The definition of ℓ_A is the same as that used previously for attached redox couples [3,4] – i.e., ℓ_A is the distance between the carbon atom attached to the sulfur and the attached atom of the redox couple so that $\ell_A = 0$ corresponds to a direct covalent connection of the sulfur to the couple.

For a redox couple in solution in contact with a SAM that is not electroactive, the standard ET rate constant ($k_S^0(\ell_S)$; units: cm s^{-1}) is defined by [12,13]

$$k_S^0(\ell_S) = k_S^0(0)\exp[-\beta_B\ell_S]\int_{x=0}^{\infty}\exp[-\beta_S x]\,dx \tag{2}$$

where $k_S^0(0)$ includes the effect of the non-covalent contact between the SAM and the redox species on the electronic coupling, x is the distance between the plane defined by the solution-side surface of the SAM and a parallel plane farther out in the electrolyte solution, and we also assume that the electron-transfer through the SAM and through the solution is nonadiabatic. (The redox species are presumably fully solvated so that the solvation shell is a component of the non-covalent contact distance between the SAM and the redox species.) Note that Eq. (2) is based on the assumptions that: (1) the only difference between attached redox moieties and redox moieties in solution is that the latter are uniformly distributed through the solution; (2) the activation energy associated with a redox couple in solution is not a function of x; and (3) there is no adsorption of the solution-dissolved redox moieties onto the solution-side surface of the SAM. In regard to the last of these assumptions, Fig. 10 in Ref. [9] demonstrates that there is no adsorption of the $Ru(NH_3)_6^{3+/2+}$ couple onto (or into) a SAM composed of $HS(CH_2)_3OH$. Analogous to the definition of ℓ_A, ℓ_S is the distance between the first carbon atom (attached to sulfur) and the van der Waals edge of the terminal atom of a component alkanethiolate molecule of the non-electroactive SAM. The definition and value (for alkanethiol SAMs) of β_B is the same for both Eqs. (1) and (2) while β_S is the exponential decay coefficient associated with the (aqueous) solution ($\beta_S = (1.68 \pm 0.07)$ Å^{-1} [14]). (This value of β_S was measured in H_2SO_4/H_2O (25% v/v) glasses at 77 K, but it is in good agreement with recent calculations which suggest that β_S in ambient liquid water is in the 1.5–1.8 Å^{-1} range [15]. As comparisons, other measured values of β_S in organic glasses [16] and fluids [17] are in the range of 1.00–1.62 Å^{-1}.) From Eq. (2)

$$k_S^0(\ell_S) = \frac{k_S^0(0)\exp[-\beta_B\ell_S]}{\beta_S} \tag{3}$$

Eqs. (1) and (3) permit a direct comparison of the standard rate constants measured for an attached (as a constituent of a SAM) redox couple with that of a similar redox couple dissolved in an electrolyte solution in contact with the same type of (but non-electroactive) SAM. We define a comparison parameter (P_c) as

$$P_c = \frac{k_A^0(0)}{k_S^0(0)} = \frac{k_A^0(\ell_A)\exp[\beta_B(\ell_A - \ell_S)]}{\beta_S k_S^0(\ell_S)} \tag{4}$$

Eq. (4), in effect, normalizes the ET rates of covalently attached and (similar) solution-dissolved redox couples to each other. We emphasize that the parameter P_c focuses on a single interfacial contact for both the attached and solution-dissolved redox couples. The parameter P_c, therefore, is a measure of any difference between the covalent connection associated with an attached redox couple and the analogous case involving a non-covalent linkage, where $k_S(0)$ corresponds to a non-covalent contact between a SAM and a redox species. If the characteristics of these two junctions are the same with respect to electron-transfer, the value of P_c should be unity.

3. Results and discussion

Table 1 contains values of P_c calculated using Eq. (4) and data from four systems (where different alkanethiol SAMs refer to different numbers of CH_2 groups of the constituent molecules of the SAMs):

(1) covalently attached ferrocenyl ($(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$–) as a constituent of two alkanethiol SAMs [3,18];
(2) $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)\text{-}CH_2\text{-}N(CH_3)_3^{2+/+}$ (i.e., Fc-$CH_2N(CH_3)_3^{2+/+}$, where Fc denotes the ferrocenyl group) dissolved in electrolyte solutions in contact with an ω-hydroxythiol SAM [20] or an alkanethiol SAM [21];
(3) (pyridinyl)$Ru(NH_3)_5^{3+/2+}$ covalently attached through the pyridinyl to ω-carboxylic acid alkanethiol SAMs [3,19];
(4) $Ru(NH_3)_6^{3+/2+}$ dissolved in electrolyte solutions in contact with three different ω-hydroxyalkanethiol SAMs [9,20,22].