Reduction of Ferricyanide by Methylene Blue at a DNA-Modified Rotating-Disk Electrode

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Abstract:

The electrocatalytic reduction of ferricyanide mediated by methylene blue (MB) at a DNA-modified electrode was investigated by linear-sweep voltammetry at a rotating-gold-disk electrode (RDE). Electrodes were modified with thiol-terminated double-stranded oligonucleotides (sequence: 5'-SH-AGTACAGTCATCCGC-3') to form densely packed DNA films that blocked the electrochemical reduction of millimolar solutions of ferricyanide at overpotentials greater than 0.5 V. Addition of micromolar concentrations of MB to these solutions, however, resulted in the rapid appearance of catalytic currents as long as the potential was held negative of the formal potential of MB within the DNA film (-0.30 V vs SCE). MB binds reversibly to these DNA-modified surfaces, and the adsorption kinetics of MB were determined by a coulometric assay. These data fit a simple Langmuir model with k_1 (adsorption) = 7.5(6) × 10^5 M^{-1} s^{-1} and k_{-1} (desorption) = 0.043(8) s^{-1}. Interestingly, linear-sweep RDE voltammograms recorded in the presence of MB revealed "peaked"-shaped *i*-*V* traces, which took several seconds to reach their steady-state values. Moreover, the steady-state current density for reduction of $Fe(CN)_6^{3-}$ was found to depend on the bulk concentration of MB in solution. A model is proposed to account for these data in which $Fe(CN)_6^{3-}$ turnover is limited ultimately by the kinetics of MB crossing into and out of the film, and the chemical reaction between $Fe(CN)_6^{3-}$ and reduced MB occurs at the film/solution interface.