Differential Ionic Permeation of DNA-Modified Electrodes

Donato M. Ceres,† Andrew K. Udit,‡ Haley D. Hill,‡ Michael G. Hill,*‡ and Jacqueline K. Barton*†

Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, and Department of Chemistry, Occidental College, Los Angeles, California 90041

Received: September 26, 2006

In Final Form: November 10, 2006

Abstract:

Ionic permselectivity of DNA films has been investigated by the analysis of the electrochemical response of methylene blue (MB) as a function of pH and ionic strength on DNA-modified electrodes in aqueous *p*-nitrophenol (*p*-NP) and phosphate buffers. We have observed a linear Pourbaix diagram in *p*-NP buffer indicating that the reduction of MB occurs with a two-electron plus one-proton reaction. Interestingly, in phosphate buffer the Pourbaix diagram is curved and this suggests that the thermodynamics of MB incorporated in the film depend also on the ratio of mono- versus divalent anions in the bulk. This result indicates that DNA films do not behave as pure ion-exclusion films, but instead there is a differential permselectivity that depends on the identity of the anions. Based on this consideration of the ionic distribution in the films, we provide a new method for the analysis of the DNA surface coverage based on AC impedance of an anionic species, ferricyanide. The methodology is of particular value in analyzing DNA hybridization and dehybridization. This approach presents an advantage compared to standard ruthenium hexammine assays since our methodology is insensitive to film morphology, and is highly sensitive to the amount of negative charge on the surface.