

Potential Dependant Phase Transition in Surfactant Film-modified Electrodes

Emek Blair and Patrick J. Farmer

Department of Chemistry, University of California, Irvine
Irvine, CA, 92697-2025
eblair@uci.edu

Dimethyldidodecylammonium bromide (DDAB) is an ionic surfactant that is commonly used to modify electrode surfaces; it is especially applicable to the electrochemistry of proteins such as myoglobin (Mb),^{1,2} hemoglobin and cytochrome P450s.^{3,4,5} We, and others, have used these protein/DDAB electrodes as electrocatalysts to reduce nitrite,^{6,7} NO,^{8,9} N₂O,¹⁰ and alkyl halides and have examined their use as biosensors.¹¹

In this methodology, a protein sample is cast with a micellar solution of DDAB to form a thin film ca. 1 μm thick. The electrochemical response of Mb in such a film is greatly enhanced compared to that of Mb in solution, and the Fe(III/II) couple exhibits scan-rate dependence indicative of Mb diffusion through the surfactant film. A number of spectroscopic techniques indicate that Mb retains its native structure within the film environment, but we have long been puzzled by the certain aspects of its electrochemical behavior.¹²

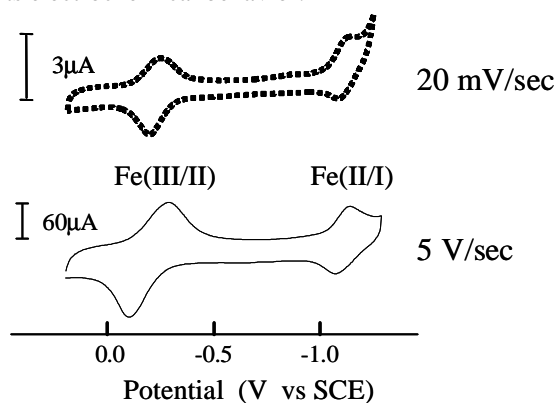


Figure 1. Cyclic voltammogram of Mb/DDAB film. The film was scanned at 500 mV/s in a 50 mM pH 8.5 iP buffer with 20 mM KCl as electrolyte using a Pt wire counter electrode and Ag/AgCl reference electrode.

As illustrated in Figure 1, the heme center in Mb is seen to undergo two reductions at the Fe(III/II) and Fe(II/I) couples. Logically, these two couples should have similar currents, but under certain conditions the current at the Fe(II/I) is clearly much smaller.¹¹ A current difference of ca 50% is seen at slow scan-rates which should access all of the redox active Mb within the film. Also, the shape of more negative voltammetric peaks is distinct from that of more positive peaks.⁶ Current vs. scan rate analysis show that the Fe(III/II) is diffusional above 500 mV/sec, but the expected diffusional current after the peak is absent; the Fe(II/I) couple has invariant small peak-to-peak separations as expected for a surface-absorbed species, but the amount of Mb that is electrochemically active is much decreased at higher scan rates. Similar behavior is seen for heme centers of peroxidases and cytochrome P450s, thus is a characteristic of the film and not the redox species.

Previous models have postulated that broadening Fe(III/II) wave of Mb/DDAB is due to a mixture of electroactive conformers in the diffusion layer.^{1,2} More recently, Boussaad *et al* described the apparent freezing at negative potentials of DDAB sub-monolayers on highly ordered pyrolytic graphite (HOPG) during AFM experiments.¹³ Our analysis of both scan rate and range

behavior suggest a liquid-to-gel phase transition occurs during voltammetric scanning past -200 mV; the “freezing” of the film at negative potentials produces the variation and unusual response of the two redox couples.

In order to directly observe the affect of potential on the surfactant/electrode interface, we have performed electrochemical quartz-crystal microbalance (EQCM) experiments that illustrate the potential-dependent change. A phase transition ca. -200 mV, is seen as a large increase in film resistance at lower potentials; the overall mass of the film remains stable, but the resistance rises due to a decreased mass transport in the gel phase, Figure 2.

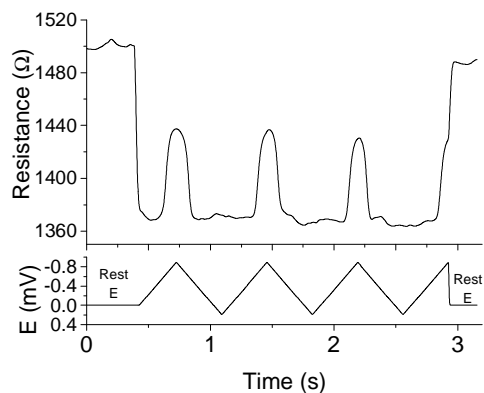


Figure 2. Film resistance during cyclic voltammetry: The potential is scanned at 50 mV/s in pure water (18 Ω) using a polished Au electrode, a Pt wire counter electrode and Ag/AgCl reference electrode.

The dynamic nature of DDAB has profound affects on the electrochemical behavior and must be considered when using this method to characterize the redox behaviors of immobilized proteins.

¹ Rusling, J.F.; Nassar, A.E.F. *J. Am. Chem. Soc.* **1993**, 115, 11891-11897.

² Nassar, A.E.F.; Narikiyo, Y.; Sagara, T.; Nakashima, N.; Rusling, J.F.; *J. Chem. Soc.-Faraday Trans.* **1995**, 91, 1775-1782.

³ Zhang, Zhe; Nassar, Alaa-Eldin F.; Lu, Zhongqing; Schenkman, John B.; Rusling, James F. *J. Chem. Soc., Faraday Trans.* **1997**, 93(9), 1769-1774.

⁴ Iwuoha, Emmanuel I.; Kane, Stephen; Ania, Conchita Ovin; Smyth, Malcolm R.; De Montellano, Paul R. Ortiz; Fuhr, Uwe. *Electroanal.* **2000**, 12(12), 980-986.

⁵ Fleming, Barry D.; Tian, Yanni; Bell, Stephen G.; Wong, Luet-Lok; Urlacher, Vlada; Hill, H. Allen O. *Eur. J. Biochem.* **2003**, 270(20), 4082-4088.

⁶ Lin, R.; Bayachou, M.; Greaves, J.; Farmer, P.J.; *J. Am. Chem. Soc.* **1997**, 119, 12689-12690.

⁷ Mimica, D.; Zagal, J. H.; Bedioui, F.; *J. Electroanal. Chem.* **2001**, 497(1-2), 106-113.

⁸ Bayachou, M.; Lin, R.; Cho, W.; Farmer, P.J.; *J. Am. Chem. Soc.* **1998**, 120, 9888-9893.

⁹ Mimica, D.; Zagal, J. H.; Bedioui, F. *Electrochem. Comm.* **2001**, 3(8), 435-438.

¹⁰ Farmer, P.J.; Lin, R.; Bayachou, M; *Comments on Inorg. Chem.* **1998**, 20, 101-120.

¹¹ Bayachou, M.; Elkbir, L.; Farmer, P.J.; *Inorg. Chem.* **2000**, 39, 289-293.

¹² Lin, R.; Immoos, C.E.; Farmer, P.J.; *J. Biol. Inorg. Chem.* **2000**, 5, 738-747.

¹³ Boussaad, S.; Tao, N. J.; *J. Am. Chem. Soc.* **1999**, 121(18), 4510-4515.