

## Spectroelectrochemical Studies of Crosslinked Hemoglobins

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The electron transfer in alpha99 and beta82 crosslinked hemoglobins with bis(3,5-dibromosalicyl) fumarate compared to unmodified hemoglobin is studied using spectroelectrochemical methods. A rigorously oxygen free, rapid equilibrium experimental system was designed to determine the formal redox potential of the heme group as well as to measure full oxidation and reduction rates. Formal redox potentials as well as full oxidation and reduction rates were determined in the presence of hexammineruthenium(III) as mediator. The formal redox potential was found more positive for the alpha99 and more negative for the beta82 crosslinked hemoglobin compared to the unmodified hemoglobin. For all three compounds, the formal redox potentials were found sensitive to electrolyte concentration, which suggests an additional stabilization of a quaternary conformation, by salt bridges between subunits. By modulating the electrolyte concentration the rate reduction rate constants could be measured as a function of driving force. Self exchange rate constants were determined via Marcus theory. Preliminary data show that the self exchange rate of autoxidation differs between native and crosslinked hemoglobins independent of the thermodynamic driving force. Both modified compounds exhibit faster autoxidation rates than hemoglobin, a fact that suggests structure and accessibility of the heme group may influence the rates observed.