Redox-linked protein dynamics of cytochrome c probed by time-resolved surface enhanced infrared absorption spectroscopy

Nattawadee Wisitruangsakul,1,3 Ingo Zebger,1* Khoa H. Ly,1 Daniel H. Murgida,2 Sanong Ekgasit,3 and Peter Hildebrandt1*

1 Technische Universität Berlin, Institut für Chemie, Sekr. PC 14, Straße des 17. Juni 135, D-10623 Berlin, Germany
2 Departamento de Química Inorgánica, Analítica y Química Física / INQUIMAE-CONICET, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires. Ciudad Universitaria, Pab. 2, piso 1, C1428EHA-Buenos Aires, Argentina.
3 Sensor Research Unit, Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand

Content:
Description of the model for approximating the electric field strength at the protein/SAM interface.
Electric field strength at the protein/SAM interface

Fig. S1. Schematic representation of the potential distribution across the electrode/SAM/protein/solution interfaces.

Within the electrostatic model for the interfacial potential drops (Fig. S1), the electric field strength at the protein/SAM interface $E_{EF}$ is given by

(S1) \[ E_{EF} = \frac{\sigma_M}{\epsilon_0 \epsilon_r} \]

or, with

(S2) \[ \sigma_M + \sigma_C + \sigma_{RC} + \sigma_S = 0 \]

(S3) \[ E_{EF} = -\frac{\sigma_C + \sigma_{RC} + \sigma_S}{\epsilon_0 \epsilon_r} \]
where $\sigma_M$, $\sigma_C$, $\sigma_{RC}$, and $\sigma_S$ are the charge densities on the metal, on the SAM, at the reaction site (heme), and in the solution, respectively (§ref). The quantities $\varepsilon_0$ and $\varepsilon_S$ refer to the permittivity and the dielectric constant in the SAM, respectively. Linearisation of the Gouy-Chapman expression for $\sigma_S$ allows rewriting Eq. S3 to

\begin{equation}
E_{EF} = -\frac{\sigma_c + \sigma_{RC} - \varepsilon_0 \varepsilon_S \kappa E_{RC}}{\varepsilon_0 \varepsilon_c} \tag{S4}
\end{equation}

where $\varepsilon_S$ and $\kappa$ are the dielectric constant and the Debye length in solution. $E_{RC}$ denote the potential drop at the redox site which can be expressed by

\begin{equation}
E_{RC} = \frac{\varepsilon_c \varepsilon_p d_C + \varepsilon_c \varepsilon_p (E - E_{pzc}) + (d_c \varepsilon_p + d_{RC} \varepsilon_C) \sigma_{RC}}{\varepsilon_0 [\varepsilon_c \varepsilon_p + (d_c \varepsilon_p + d_{RC} \varepsilon_C) \varepsilon_S \kappa]} \tag{S5}
\end{equation}

Here $\varepsilon_p$ is the dielectric constant in the protein and $d_C$ and $d_{RC}$ are the thickness of the SAM and the distance between the SAM/protein interface and the reaction site, as defined in Fig. S1. The quantities $E$ and $E_{pzc}$ refer to the electrode potential and the potential of zero charge, respectively. Inserting Eq. S5 into Eq. S4 one obtains

\begin{equation}
E_{EF} = \frac{-\sigma_c \varepsilon_p (E - E_{pzc}) - \sigma_{RC} \varepsilon_c \varepsilon_p + \varepsilon_0 \varepsilon_S \varepsilon_c \varepsilon_p \kappa (E - E_{pzc})}{\varepsilon_c \varepsilon_p + (d_c \varepsilon_p + d_{RC} \varepsilon_C) \varepsilon_S \kappa} \tag{S6}
\end{equation}

Since at pH values around 7, $|\sigma_c| \gg |\sigma_{RC}|$ and furthermore $\varepsilon_c \varepsilon_p << d_{RC} \varepsilon_c \varepsilon_S \kappa$, Eq. S6 simplifies to

\begin{equation}
E_{EF} = \frac{-\sigma_c d_{RC} + \varepsilon_0 \varepsilon_p (E - E_{pzc})}{\varepsilon_0 (d_c \varepsilon_p + d_{RC} \varepsilon_C)} \tag{S7}
\end{equation}