

Supporting Information for
**Fourier Transform Infrared Spectroelectrochemistry and Quantitative
Modeling of Analytes in Kinetically Constrained Redox Mixtures**

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Complete set of ODEs for a system with a single mediator and analyte pair.

$$\frac{dC_{\text{Ox}}^{\text{M}}}{dt} = -k_{\text{f,sol}} C_{\text{Ox}}^{\text{M}} C_{\text{Rd}}^{\text{A}} + k_{\text{r,sol}} C_{\text{Rd}}^{\text{M}} C_{\text{Ox}}^{\text{A}} - k_{\text{on}} C_{\text{Ox}}^{\text{M}} + k_{\text{off}} \Gamma_{\text{Ox}}^{\text{M}}$$

$$\frac{d\Gamma_{\text{Ox}}^{\text{M}}}{dt} = k_{\text{on}} C_{\text{Ox}}^{\text{M}} - k_{\text{off}} \Gamma_{\text{Ox}}^{\text{M}} + k_{\text{f,el}} \Gamma_{\text{Rd}}^{\text{M}} - k_{\text{r,el}} \Gamma_{\text{Ox}}^{\text{M}}$$

$$\frac{dC_{\text{Rd}}^{\text{M}}}{dt} = k_{\text{f,sol}} C_{\text{Ox}}^{\text{M}} C_{\text{Rd}}^{\text{A}} - k_{\text{r,sol}} C_{\text{Rd}}^{\text{M}} C_{\text{Ox}}^{\text{A}} - k_{\text{on}} C_{\text{Rd}}^{\text{M}} + k_{\text{off}} \Gamma_{\text{Rd}}^{\text{M}}$$

$$\frac{d\Gamma_{\text{Rd}}^{\text{M}}}{dt} = k_{\text{on}} C_{\text{Rd}}^{\text{M}} - k_{\text{off}} \Gamma_{\text{Rd}}^{\text{M}} - k_{\text{f,el}} \Gamma_{\text{Rd}}^{\text{M}} + k_{\text{r,el}} \Gamma_{\text{Ox}}^{\text{M}}$$

$$\frac{dC_{\text{Ox}}^{\text{A}}}{dt} = k_{\text{f,sol}} C_{\text{Ox}}^{\text{M}} C_{\text{Rd}}^{\text{A}} - k_{\text{r,sol}} C_{\text{Rd}}^{\text{M}} C_{\text{Ox}}^{\text{A}} - k_{\text{on}} C_{\text{Ox}}^{\text{A}} + k_{\text{off}} \Gamma_{\text{Ox}}^{\text{A}}$$

$$\frac{d\Gamma_{\text{Ox}}^{\text{A}}}{dt} = k_{\text{on}} C_{\text{Ox}}^{\text{A}} - k_{\text{off}} \Gamma_{\text{Ox}}^{\text{A}} + k_{\text{f,el}} \Gamma_{\text{Rd}}^{\text{A}} - k_{\text{r,el}} \Gamma_{\text{Ox}}^{\text{A}}$$

$$\frac{dC_{\text{Rd}}^{\text{A}}}{dt} = -k_{\text{f,sol}} C_{\text{Ox}}^{\text{M}} C_{\text{Rd}}^{\text{A}} + k_{\text{r,sol}} C_{\text{Rd}}^{\text{M}} C_{\text{Ox}}^{\text{A}} - k_{\text{on}} C_{\text{Rd}}^{\text{A}} + k_{\text{off}} \Gamma_{\text{Rd}}^{\text{A}}$$

$$\frac{d\Gamma_{\text{Rd}}^{\text{A}}}{dt} = k_{\text{on}} C_{\text{Rd}}^{\text{A}} - k_{\text{off}} \Gamma_{\text{Rd}}^{\text{A}} - k_{\text{f,el}} \Gamma_{\text{Rd}}^{\text{A}} + k_{\text{r,el}} \Gamma_{\text{Ox}}^{\text{A}}$$

Runge-Kutta boundary conditions: The concentration C (or Γ) of any component in any phase was

allowed to rise or fall over the complete step Δt to maintain relative change $\Delta_{\Delta t} C = \frac{C_{t+\Delta t} - C_t}{C_t}$ within the

limits of $0.5 \leq \Delta_{\Delta t} C \leq 5$. Relative changes over intermediate sub-steps of Runge-Kutta integration were

afforded wider boundary conditions of $0.8 \leq \Delta_{\Delta t} C \leq 100$. If the boundary conditions were violated over

either the intermediate or total step, Δt was iteratively reduced by 90% and the simulation step restarted

until restrictions were met. If the boundary conditions in the preceding step were satisfied, the next Δt

was increased by 25%.

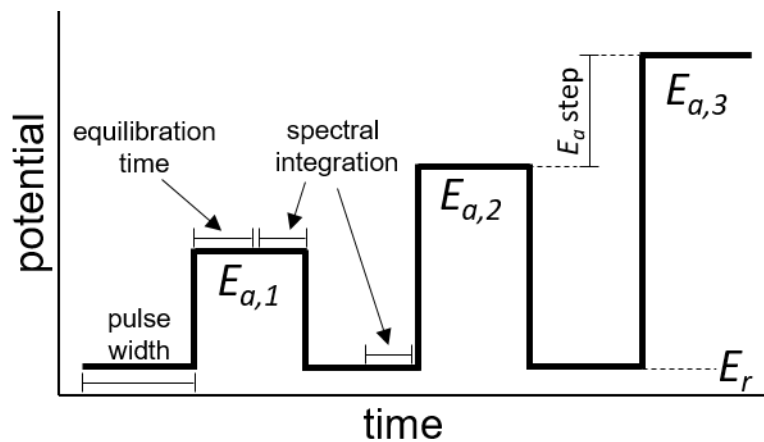


Figure S-1. Potential profile of NPSV. E_a alternates between a constant reference, E_r , and variable applied, $E_{a,i}$, potentials over successive cycles.

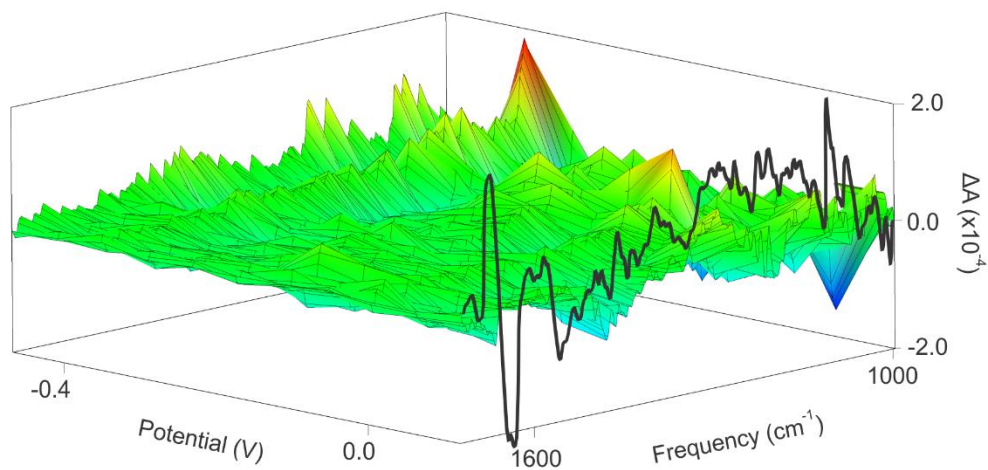


Figure S-2. Residual error from NPSV/GSR of Mb. The full occupancy spectrum of Mb is shown for reference.

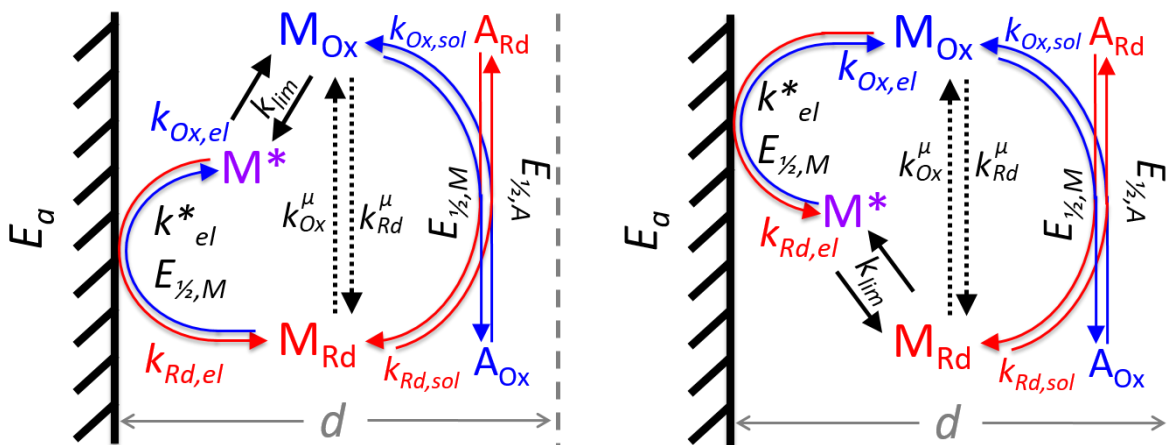


Figure S-3. Complete depiction of the reduced kinetic model showing how M^* can represent $M_{el,Ox}$ or $M_{el,Rd}$ and k_{lim} is the rate constant of the rate limiting step between M^* and either M_{Ox} or M_{Rd} .

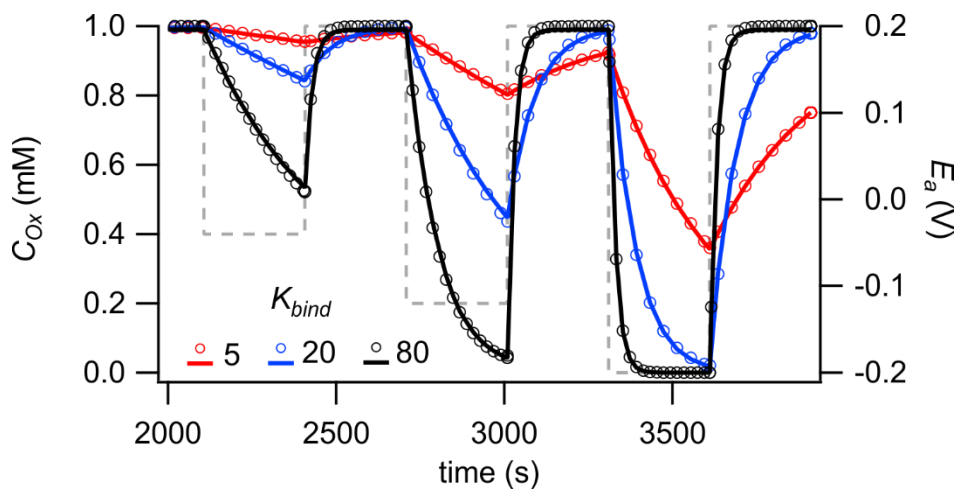


Figure S-4. Comparison of NPV concentration profiles of a single analyte calculated by the complete and reduced models (Fig. 4). Complete model simulations (solid lines) at various K_{bind} , as indicated, and constant k_{el}^o of $0.1 \text{ M}^{-1}\text{s}^{-1}$. The simplified model (open circles) used same parameters in the empirical relationship: $k_{el}^* = k_{el}^o \times (K_{bind}) \times h$ where $k_{el}^o = 0.1 \text{ M}^{-1}\text{s}^{-1}$, the layer thickness (h) was $12 \text{ }\mu\text{m}$, and $k_{lim} = k_{on}$.

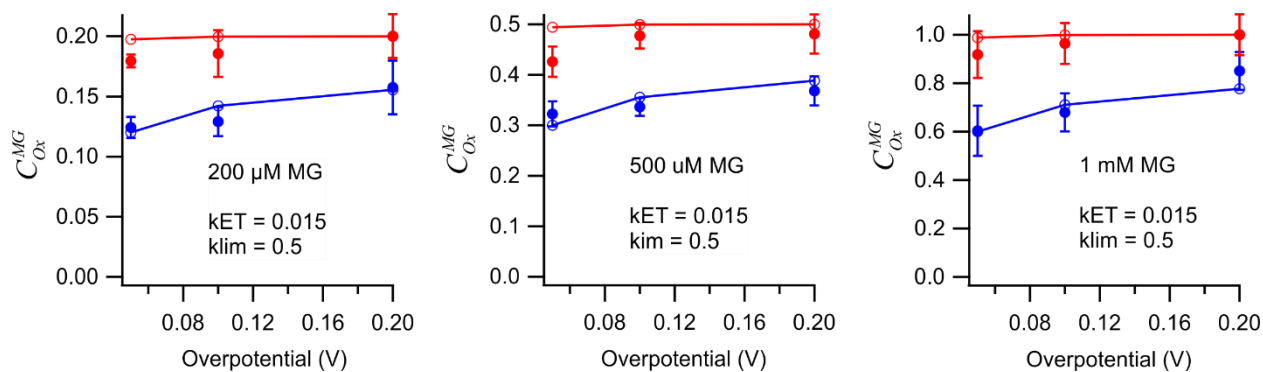


Figure S-5. Determination of k_{lim} and k_{el}^* of MG at high concentrations. MG samples were prepared in 25 mM Tris, pD 7.0, 0.5 M KCl and transferred to the OTTLE cell for FTIR measurements. MG samples were exposed to 50 mV, 100 mV, and 200 mV overpotentials over 15 s (blue) and 30 s (red) steps. IR spectra were integrated for 15 s. The intensity at 1603 cm^{-1} was normalized to the intensity of the completely oxidized sample at the same frequency and then multiplied by the concentration of the sample. Experimental data (\bullet , \bullet) were simulated ($-\circ-$, $-\circ-$) by adjusting the values of k_{lim} and k_{el}^* to find the best fit.

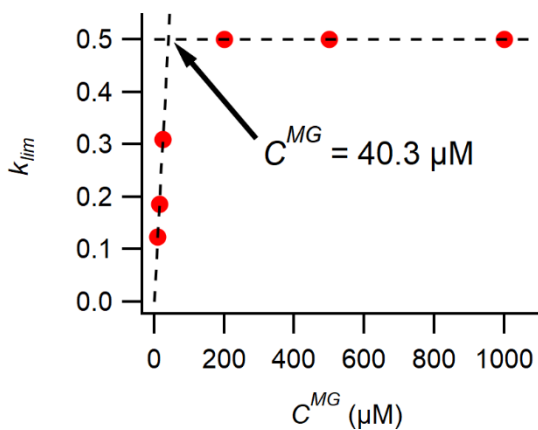


Figure S-6. k_{lim} values for MG determined at various concentrations. k_{lim} follows a linear profile at low mediator concentrations and reaches a constant value of 0.5 at $40.3\text{ }\mu\text{M}$ MG.

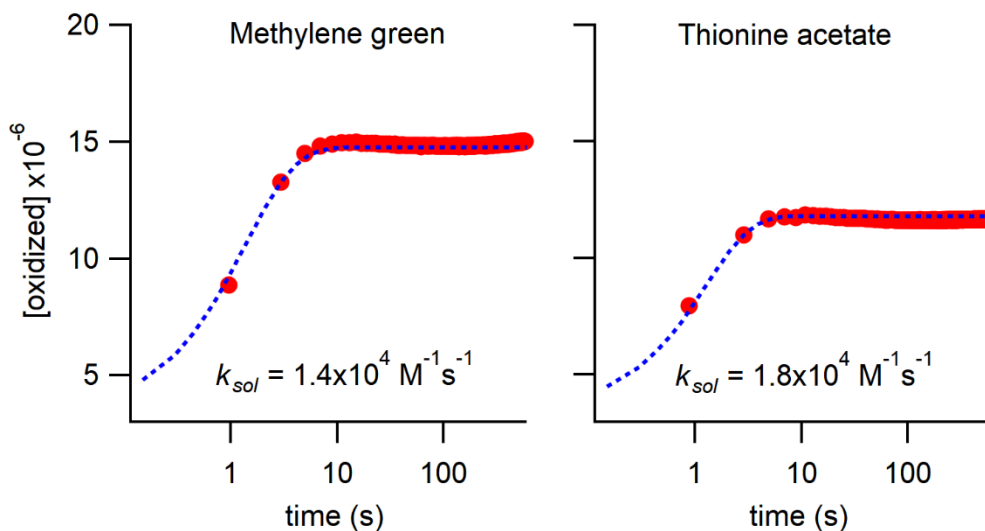


Figure S-7. Determination of homogenous bimolecular rates of reactions between mediators and Mb. Optical changes at characteristic wavelengths were recorded in 2 s intervals as a 0.5 molar equivalent of Mb was added to the reduced MG or TA. Absorbance profiles were taken from 611 nm and 598 nm for MG and TA, respectively, and converted to concentrations using their corresponding ϵ . The quantitative model was used to find the best k_{sol} value to simulate (---) the experimental (•) concentration profiles.

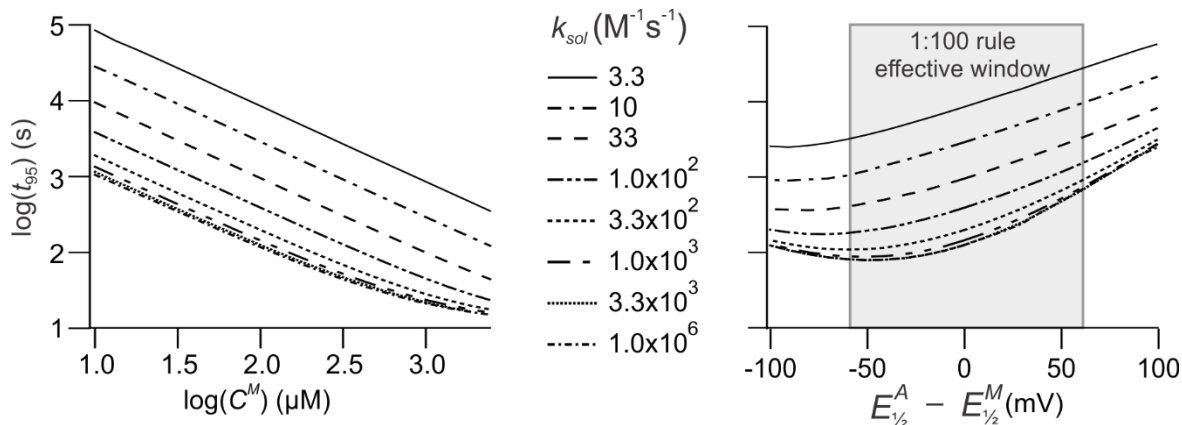


Figure S-8. The role of mediator in determining the minimum NPSV pulse duration. The minimal pulse duration (t_{95}) is calculated for of an arbitrary 1 mM analyte with k_{el}^* of 0.1 and k_{lim} of 0.4 following a potential step of $E_a = E_{1/2}^A + 100$ mV in the presence of a mediator with given bimolecular rate constant k_{sol} . *Left:* the effect of mediator concentration at $E_{1/2}^A = E_{1/2}^M$. *Right:* the effect of $E_{1/2}^M$ relative to $E_{1/2}^A$ for a constant mediator concentration of 100 μ M.