

# Kinetics of Rapid Electron Transfer Reactions at Nanoelectrodes

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## SUPPORTING INFORMATION`

### Analysis of steady-state SECM voltammograms

Two approximate theoretical expressions were used in ref. S1 to extract kinetic parameters from steady-state tip voltammograms, assuming quasi-reversible Butler-Volmer ET kinetics, i.e., Eq. (19)

$$i_T/i_{T,\infty} = [0.68 + 0.78377/L + 0.3315\exp(-1.0672/L)]/(\theta + 1/\kappa) \quad (S1)$$

and Eq. (25)

$$i_T = \frac{0.78377}{L(\theta + 1/\kappa_{TLC})} + \frac{0.68 + 0.3315\exp(-1.0672/L)}{\theta[1 + \frac{\pi}{\kappa'\theta} \frac{2\kappa'\theta + 3\pi}{4\kappa'\theta + 3\pi^2}]} \quad (S2)$$

where the dimensionless kinetic parameters are  $\kappa = k^\circ \exp[-\alpha n f(E - E^\circ)]/m_O$ ,

$\kappa_{TLC} = 4\kappa'D_O/(\pi a m_{TLC})$ , and  $\kappa' = \pi a k^\circ \exp[-\alpha n f(E - E^\circ)]/(4D_O)$ ;

$m_O = 4D_O(0.68 + 0.78377/L + 0.3315\exp(-1.0672/L))/(\pi a)$  is the effective mass transfer

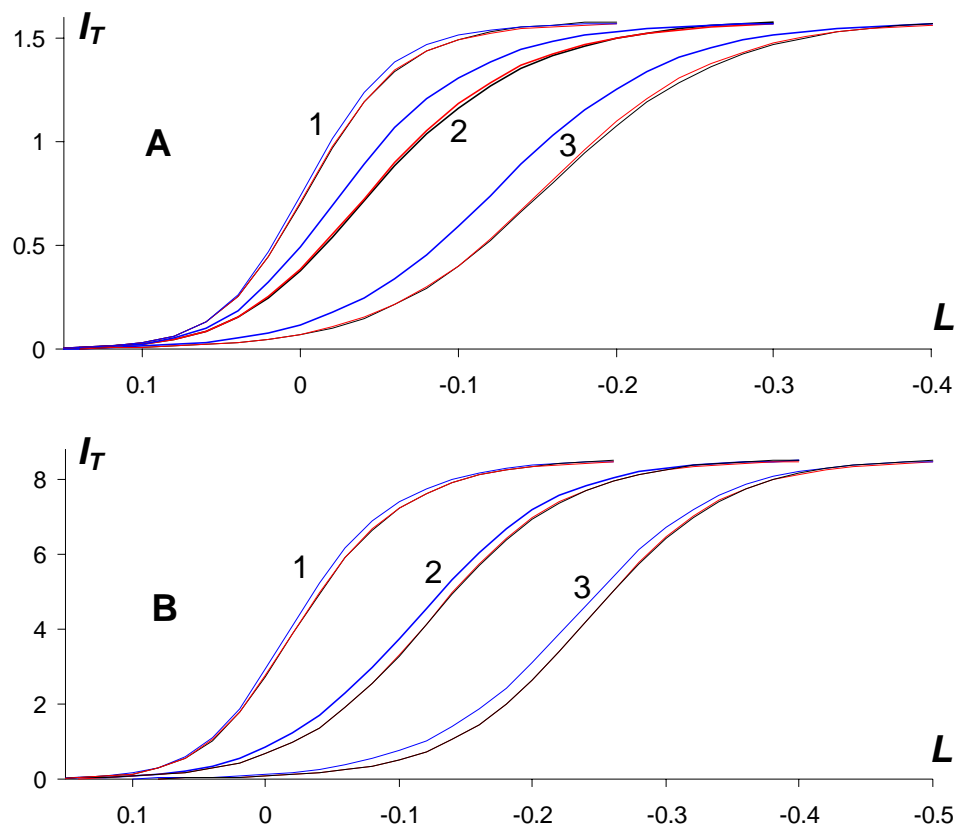
coefficient for SECM,  $m_{TLC} = \frac{2D_OD_R}{(D_O + D_R)d}$  is the effective mass transfer for a thin layer

cell, and  $\theta = 1 + \exp[nf(E - E^\circ)]D_O/D_R$ .

Unlike Eq. (S2), Eq. (S1) was obtained assuming uniform accessibility of the tip surface, but the differences between kinetic parameters obtained using those equations were not large.<sup>S1</sup> Since neither Eq. (S1) nor Eq. (S2) has previously been checked against the exact solution of the SECM diffusion problem, we compared the voltammograms calculated from those equations to the data produced by numerical simulations. Quasi-reversible SECM tip voltammograms were calculated using FEMLAB finite element simulation package (version 3.1 with Chemical Engineering Module).<sup>S2</sup> We compared the results of FEMLAB simulations to available exact theory and previously verified analytical approximations for diffusion limiting SECM currents and for quasi-reversible ET at a microdisk electrode and found the relative error to be <1% in all cases. Since this error is smaller than the experimental uncertainty, the simulated data can be considered “exact” for all practical purposes.

Steady-state voltammograms computed for different values of the kinetic parameter  $\lambda$  ( $\lambda = k^0 a/D$ , where  $D$  is the diffusion coefficient of the redox species) and tip/substrate separation distances are shown in Figure S1. The magnitude of the difference between the blue curves calculated from Eq. (S2) and the simulated voltammograms (black curves) depends on both  $\lambda$  and  $L$  values. At larger  $L$  (e.g.,  $L = 1$  in Fig. S1A), the relative error of several per cent in the calculated current may result in a significantly underestimated value of the standard rate constant. The difference between the corresponding blue and black curves gets smaller with increasing  $\lambda$  (i.e., from the group of curves labeled 3 to the group labeled 1). However, one should notice that the faster the ET rate the more sensitive the value of the extracted rate constant to the shape of the steady-state voltammogram. For smaller  $L$  (e.g.,  $L = 0.1$  in Fig. S1B), the

deviations of calculated voltammograms from the numerical solution are smaller, yet large enough to produce significant errors in extracted kinetic parameters. Although Eq. (S1) is somewhat more accurate than Eq. (S2) (the data not shown), the voltammograms obtained from it at larger  $L$  still deviate from the exact solution.



**Figure S1.** Analytical approximations for quasi-reversible tip voltammograms and diffusion-controlled mediator regeneration at the SECM substrate. The curves were obtained from: Eq. (S2) (blue), Eq. (3) (red), and FEMLAB simulations (black).  $L = 1$  (A) and  $0.1$  (B).  $\lambda = 10$  (1),  $1$  (2), and  $0.1$  (3).  $D_O = D_R$ .  $\alpha = 0.5$ .

By modifying Eq. (S2), we obtained a much more accurate approximation, Eq. (3) (in the main text). From Fig. S1, one can see that Eq. (3) (black curves) provides a much better fit to simulated voltammograms than Eq. (S2) at both short ( $L = 0.1$ ) and long ( $L = 1.0$ ) tip/substrate separation distances. Eq. (3) is presented in the form suitable for

reduction reactions at the SECM tip, however, with  $\kappa = \pi\lambda\exp[(1-\alpha)F(E-E^\circ)/RT]/(4I_T^c)$

and  $\theta = 1 + \exp[F(E^\circ - E)/RT]D_O/D_R$ , it is also applicable to oxidation reactions at the tip.

## References

(S1) Mirkin, M. V.; Richards, T. C.; Bard, A. J. *J. Phys. Chem.* **1993**, *97*, 7672.

(S2) FEMLAB, Version 3.1, COMSOL AB, Stockholm, Sweden, 2004.