

SUPPLEMENTARY MATERIAL

MATHCAD WORKING SHEET of a WORK

Analysis of enzyme-substrate interactions from square-wave protein-film voltammetry of complex electrochemical-catalytic mechanism associated with reversible regenerative reaction

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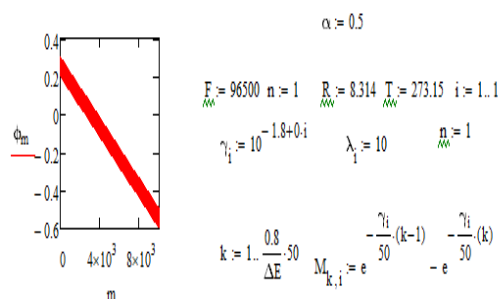
$$E_s := 0.25$$

$$\Delta E := 0.004 \quad E_{sw} := 0.05$$

$$m := 1.. \frac{0.8}{\Delta E} \cdot 50$$

$$\text{relativenpot}_m := \left[\left(\text{ceil} \left(\frac{m-1}{25} \right) \cdot \Delta E + \text{if} \left(\frac{\text{ceil} \left(\frac{m}{25} \right)}{2} = \text{ceil} \left(\frac{m-1}{25} \right), 1, -1 \right) \cdot E_{sw} + E_{sw} \right) - \Delta E \right] \quad K_{sw} := 10$$

$$\phi_m := E_s + E_{sw} - \text{relativenpot}_m$$



$$\log(\gamma_i) = \log(\lambda_i) =$$

-1.8	1
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$$\gamma_i =$$

0.0158

$$\phi_{swm} := \frac{n \cdot F}{R \cdot T} \phi_m$$

$$\Psi_{1,i} := \frac{\lambda_i \cdot e^{-\alpha \cdot \phi_1}}{1 + \lambda_i \cdot e^{-\alpha \cdot \phi_1} (1 + e^{\phi_1}) \frac{M_{1,i} \cdot K}{\gamma_i (1 + K)} + \lambda_i \cdot e^{-\alpha \cdot \phi_1} (1 + e^{\phi_1}) \frac{M_{1,i} \cdot 1}{1 \cdot (1 + K)}}$$

$$\Psi_{m,i} := \frac{\lambda_i \cdot e^{-\alpha \cdot \phi_m} \left[1 - \frac{(1 + e^{\phi_m}) \cdot K}{\gamma_i (1 + K)} \sum_{j=1}^{m-1} [\Psi_{j,i} \cdot M_{(m-j)+1,i}] - \frac{(1 + e^{\phi_m}) \cdot 1}{1 \cdot (1 + K)} \sum_{j=1}^{m-1} [\Psi_{j,i} \cdot M_{(m-j)+1,i}] \right]}{1 + \lambda_i \cdot e^{-\alpha \cdot \phi_m} (1 + e^{\phi_m}) \frac{M_{1,i} \cdot K}{\gamma_i (1 + K)} + \lambda_i \cdot e^{-\alpha \cdot \phi_m} (1 + e^{\phi_m}) \frac{M_{1,i} \cdot 1}{1 \cdot (1 + K)}}$$

Surface catalytic EC' reversible mechanism

ΔE is potential step

E_{sw} is square-wave amplitude

E_s is starting potential

m is potential counter

ϕ_m is dimensionless potential

F is Faraday constant

R is universal gas constant

T is thermodynamic temperature

γ is catalytic parameter

n is number of exchanged electrons

$\lambda = K_{et}$ - it is dimensionless parameter of electron transfer

α is electron transfer coefficient

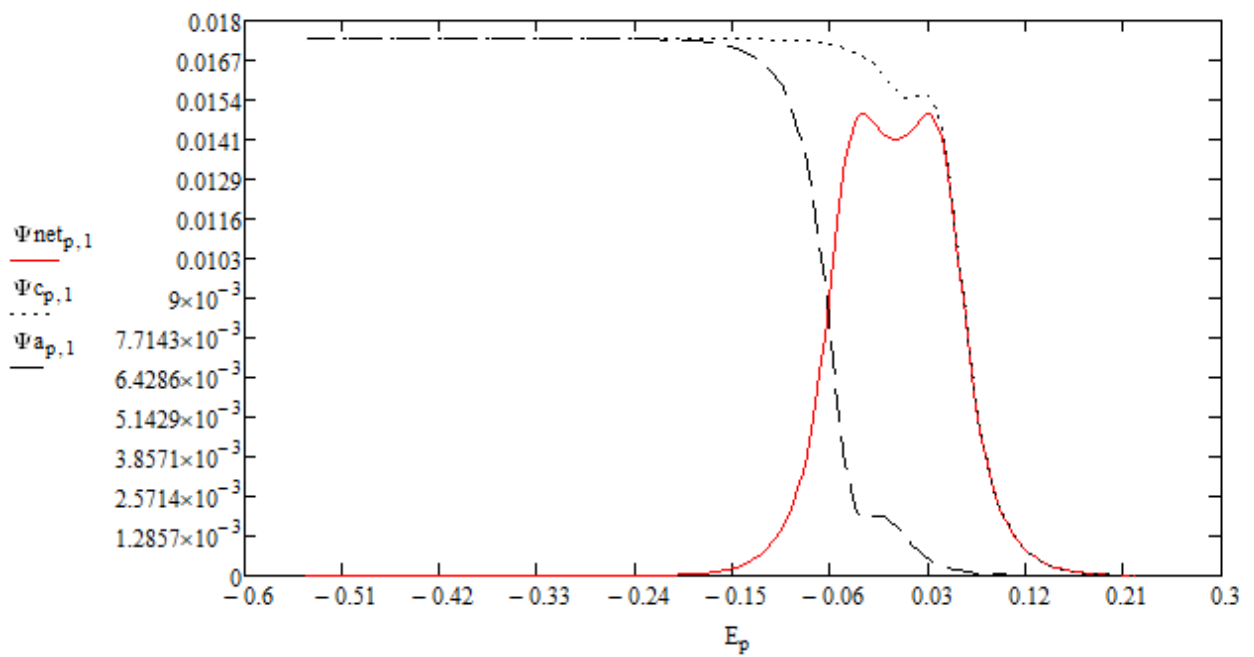
$K = K_{eq}$ - it is equilibrium constant of regenerative chemical reaction

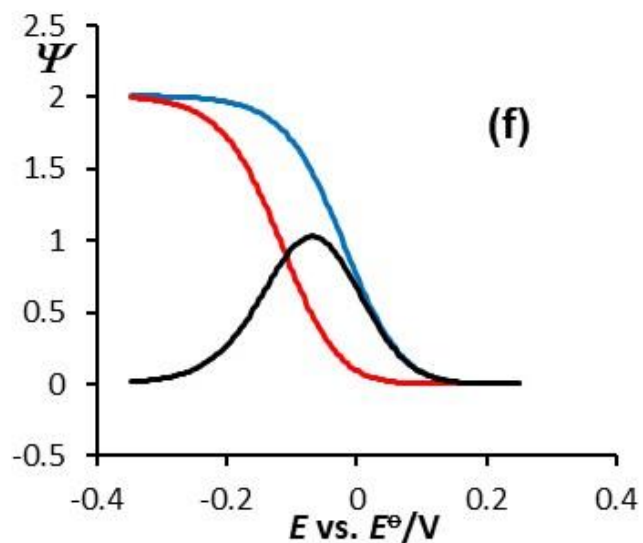
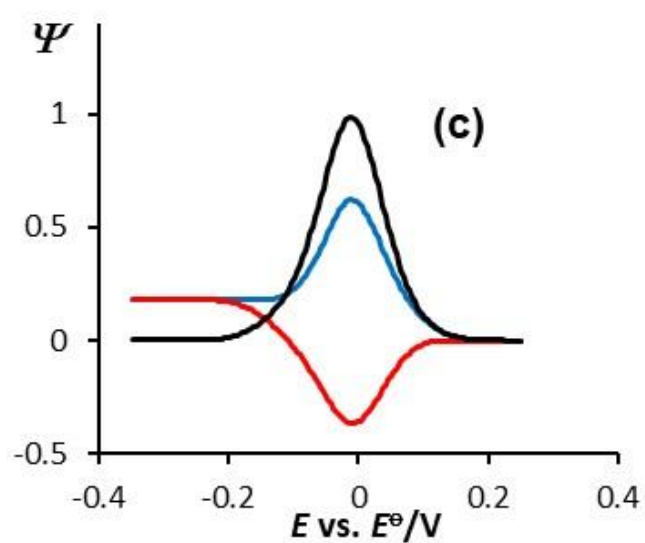
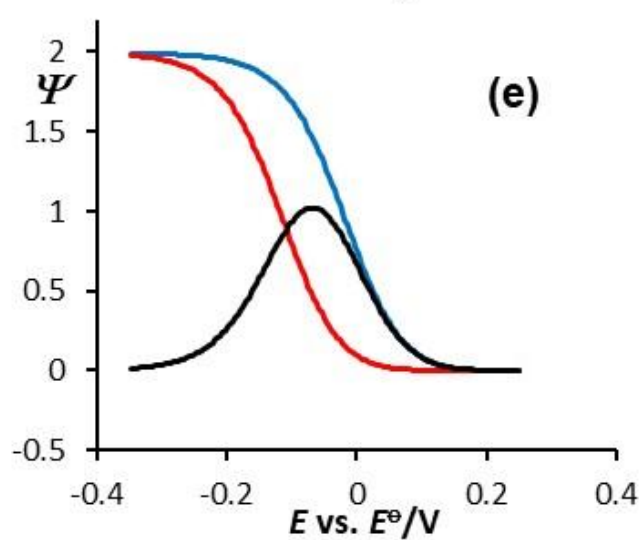
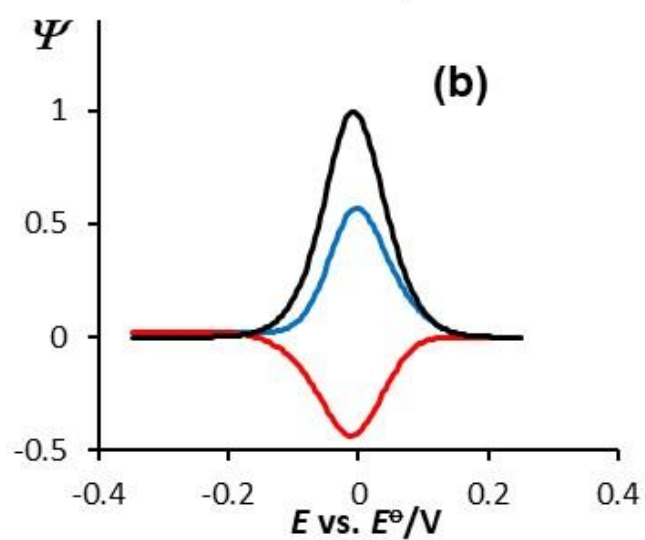
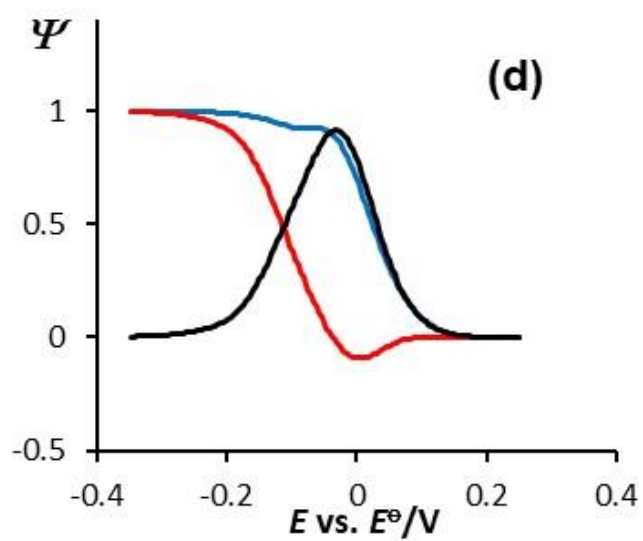
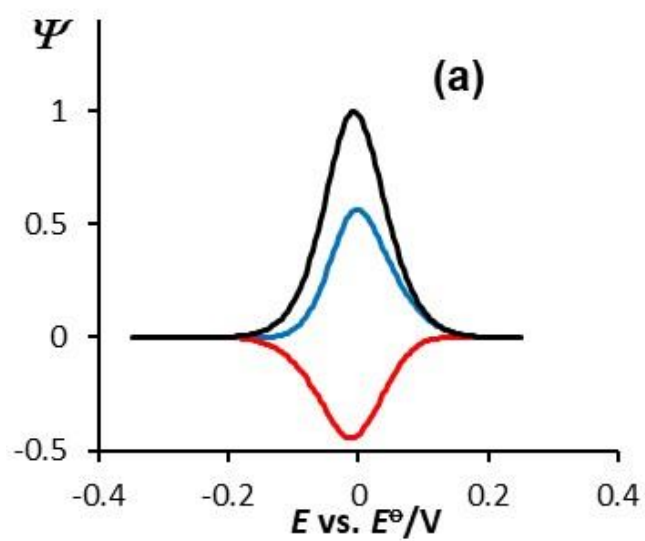
M is numerical integration factor

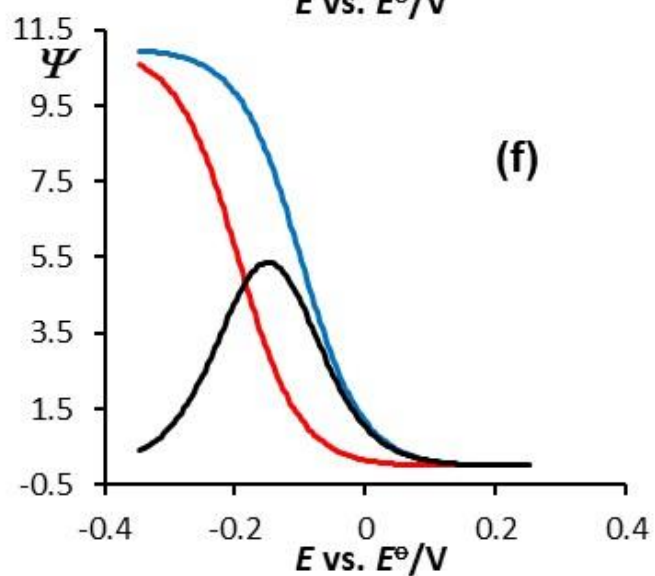
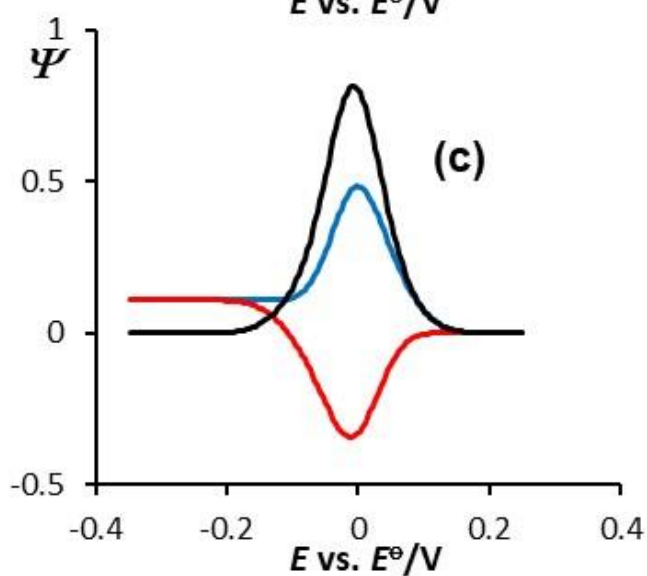
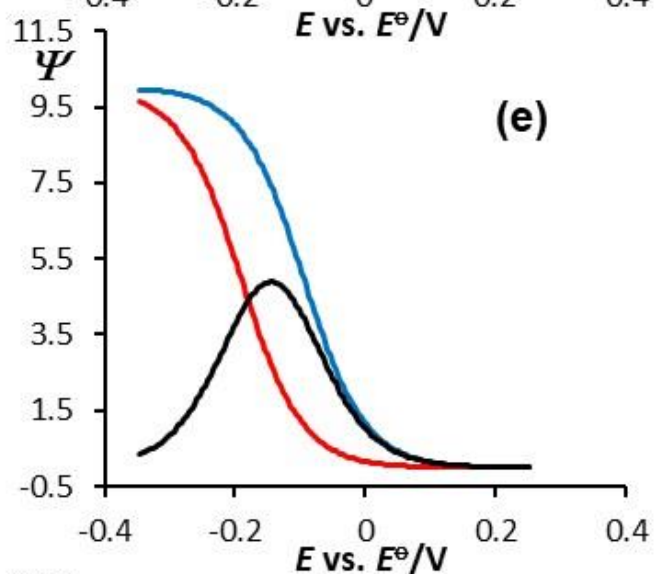
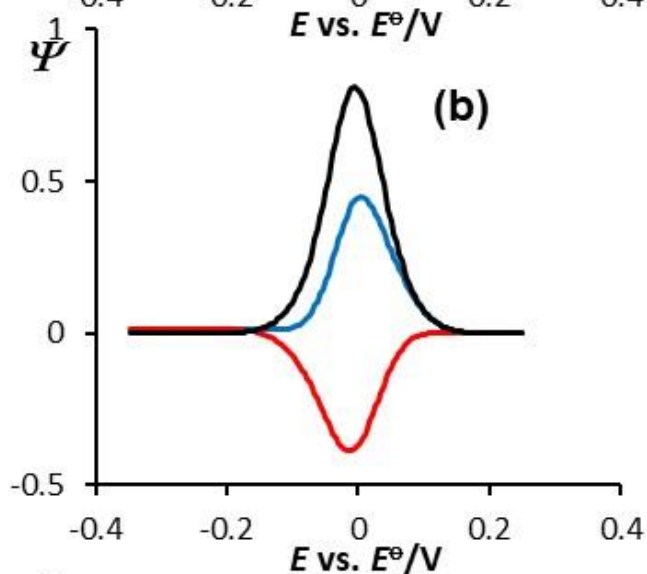
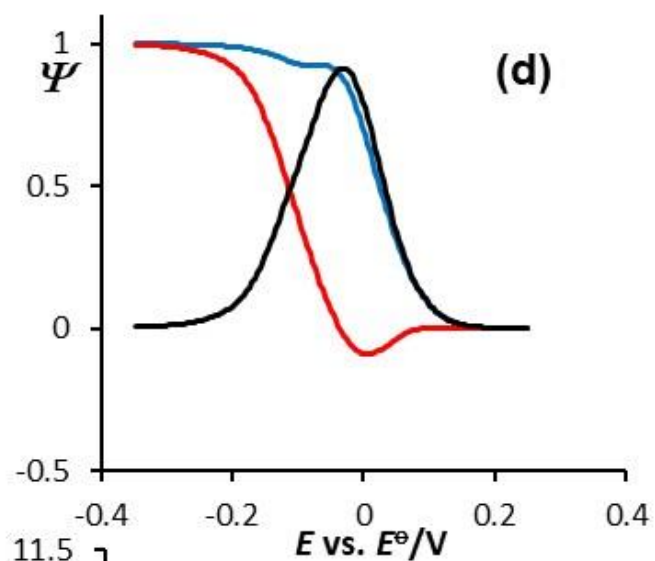
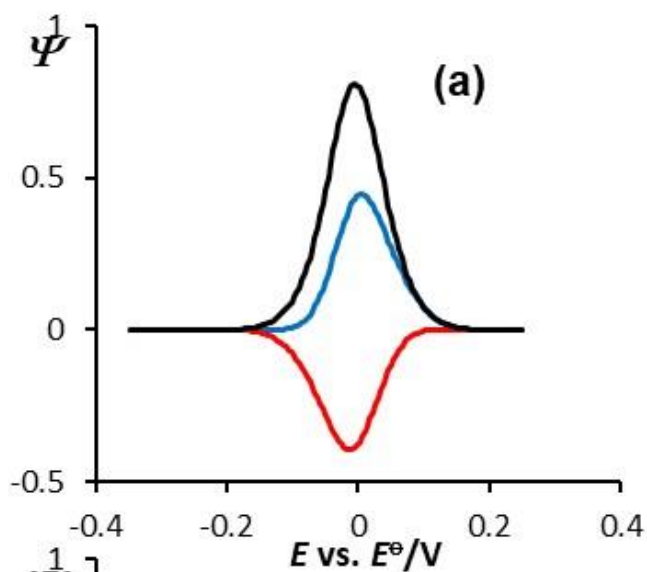
Ψ is dimensionless current

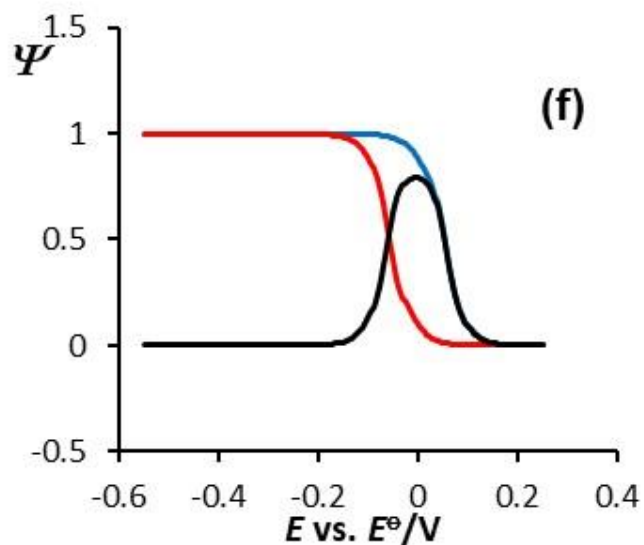
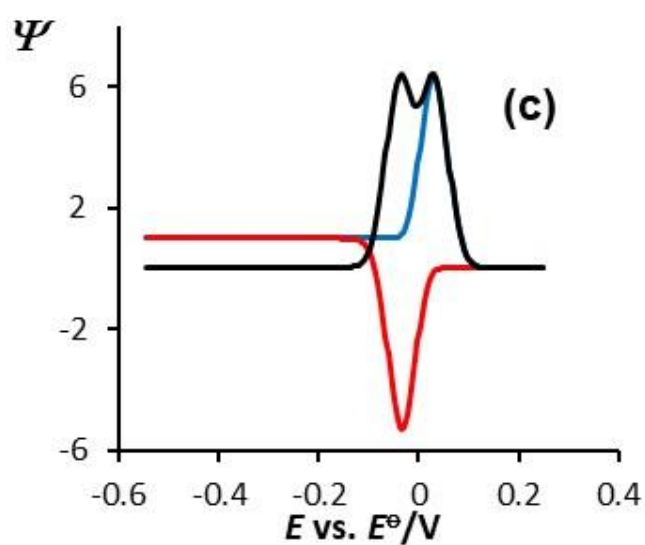
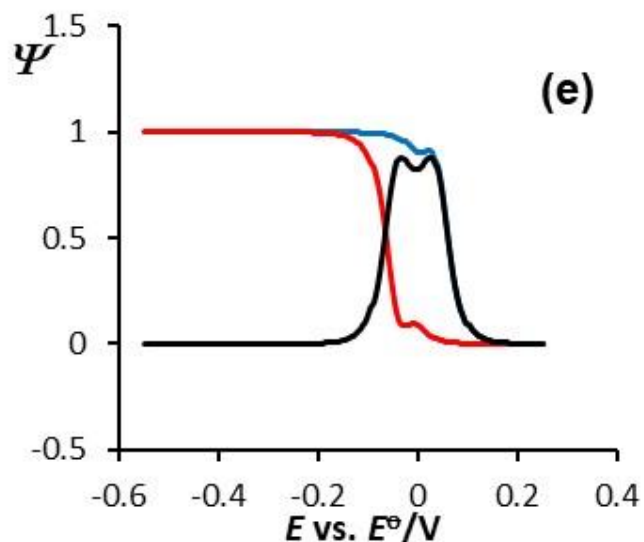
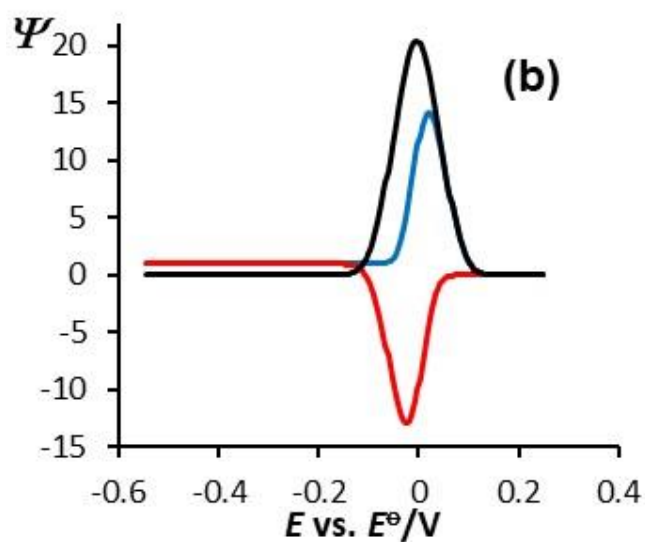
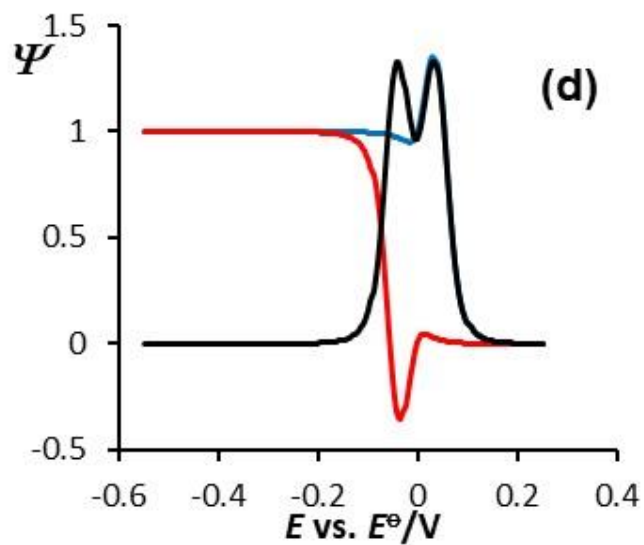
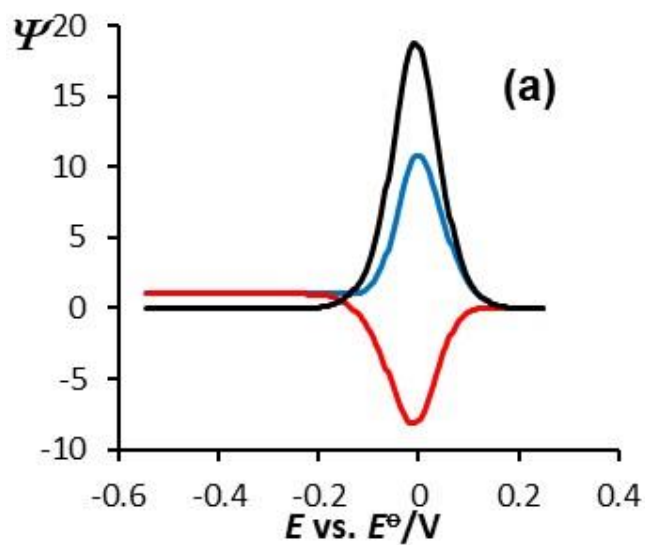
$$p := 0.8 \frac{\Delta E}{E_p} - 1 \quad E_p := E_s - p \cdot \Delta E$$

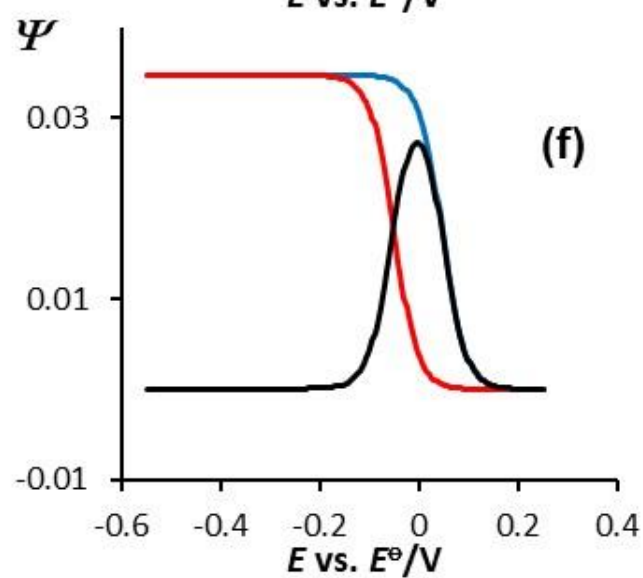
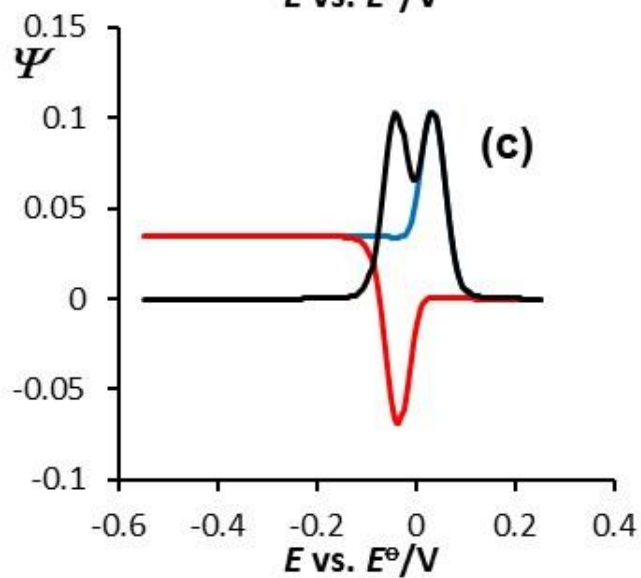
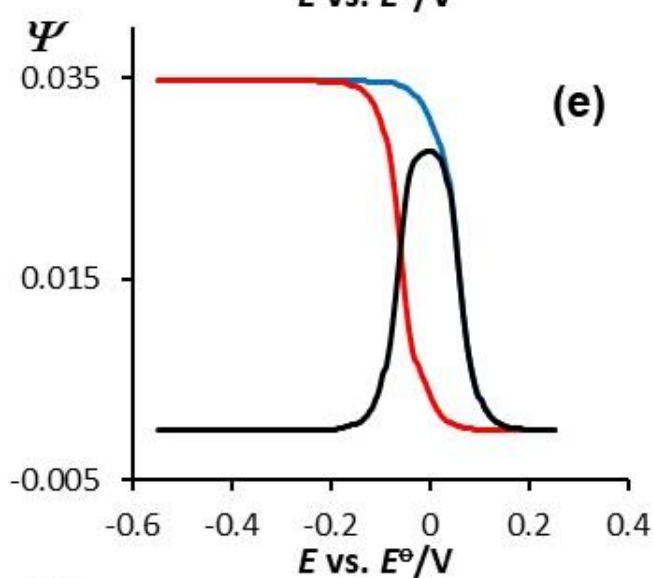
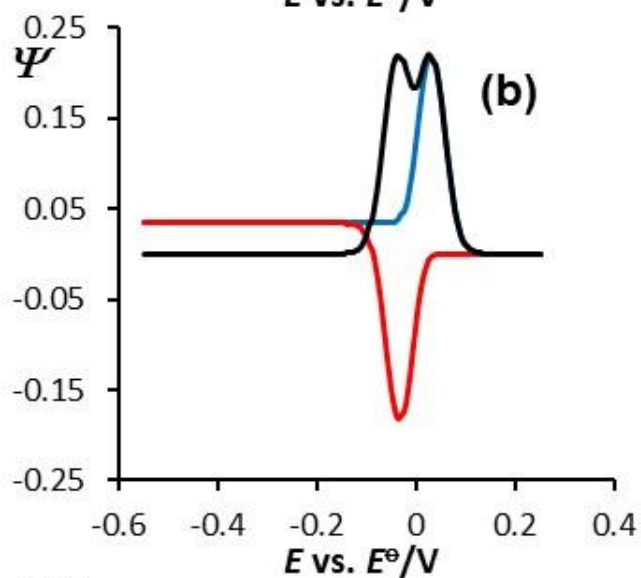
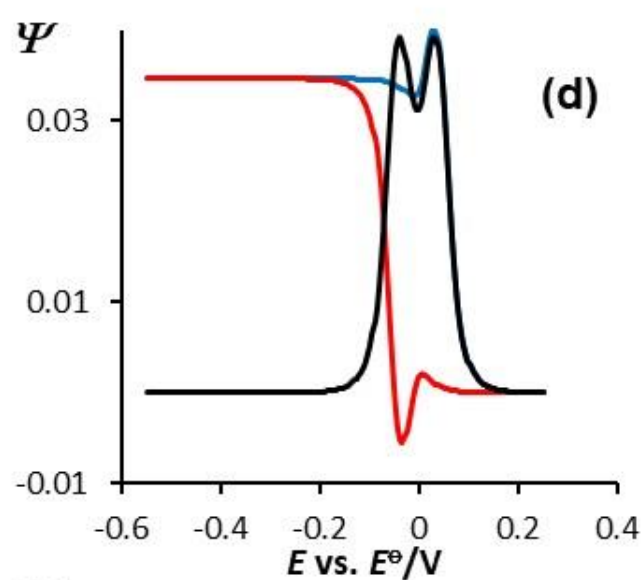
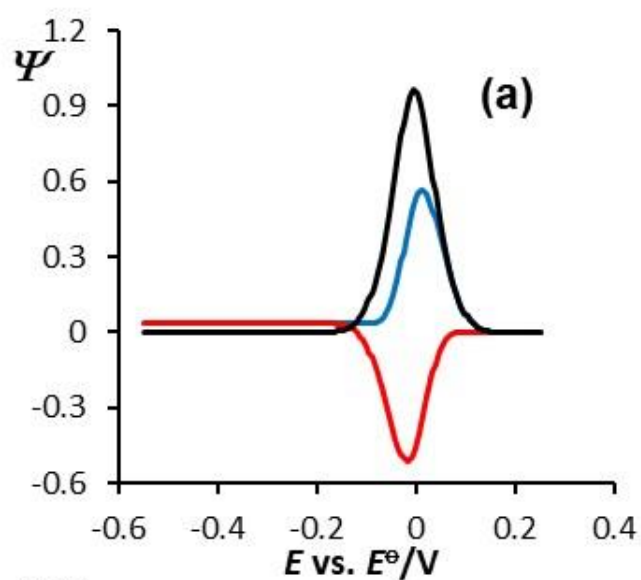
$$\Psi_{p,i}^a := \Psi_{50-p+25,i} \quad \Psi_{p,i}^c := \Psi_{(p+1) \cdot 50,i} \quad \Psi_{p,i}^{\text{net}} := \Psi_{p,i}^c - \Psi_{p,i}^a$$

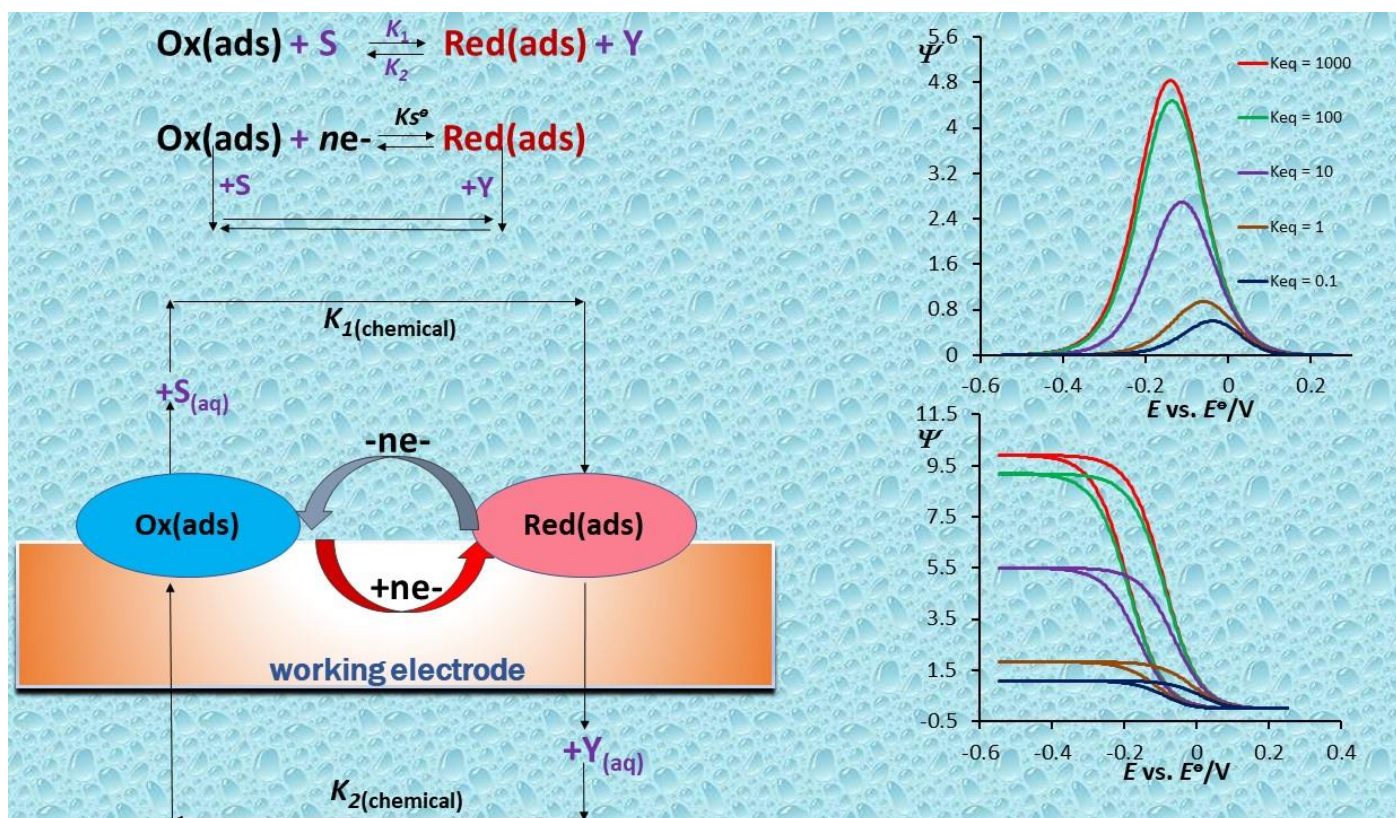












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