Fitting procedure by differential EC’ mechanism in cyclic voltammetry

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Abstract

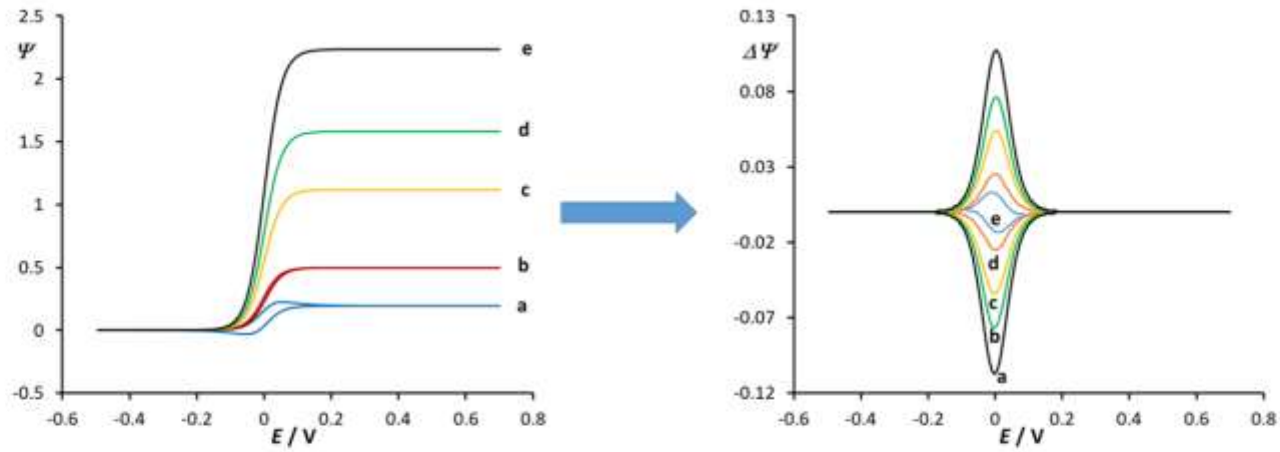
The EC′ mechanism represents one of the fundamental catalytic reaction schemes in cyclic voltammetry, in which an electrochemically generated species participates in a subsequent chemical reaction that regenerates the initial electroactive form. At sufficiently high rates of the regenerative reaction, the conventional peak-shaped cyclic voltammetric response gradually develops into a sigmoidal catalytic wave, making the extraction of kinetic information from conventional peak parameters increasingly difficult. In this work, we propose a differential fitting procedure for quantitative analysis of the diffusional EC′ mechanism in cyclic voltammetry. The approach is based on calculating the current difference between two consecutive potential points, (I_p-$I_{\{p-1\}}$), and comparing the resulting experimental differential response with the corresponding theoretical difference, (Ψp-$\Psi_{\{p-1\}}$), obtained from numerical simulations of the EC′ mechanism. Differentiation transforms the sigmoidal catalytic response into a well-defined peak-shaped profile while preserving its dependence on the kinetics of the regenerative chemical reaction. Systematic simulations demonstrate that the magnitude and shape of the differential response are strongly controlled by the dimensionless catalytic parameter and consequently by the rate constant of the regenerative step. Fitting experimental differential voltammograms to theoretically calculated profiles therefore provides a straightforward strategy for estimating the kinetics of the coupled chemical reaction. The proposed procedure extends the applicability of cyclic voltammetry to kinetic analysis of EC′ systems exhibiting pronounced steady-state- voltammetry. Procedure developed was successfully applied to obtain catalytic rate constants of several redox systems.

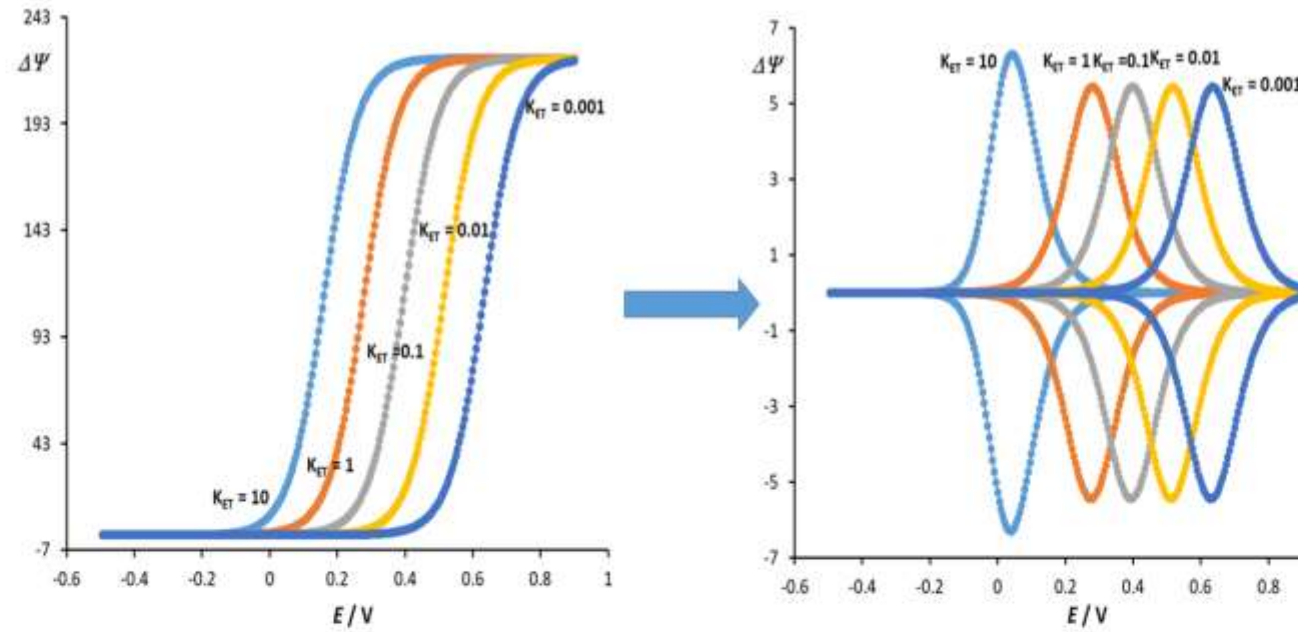
DIFFUSIONAL EC' Mechanism---differentiation method to transform steady state to peak form voltammogram

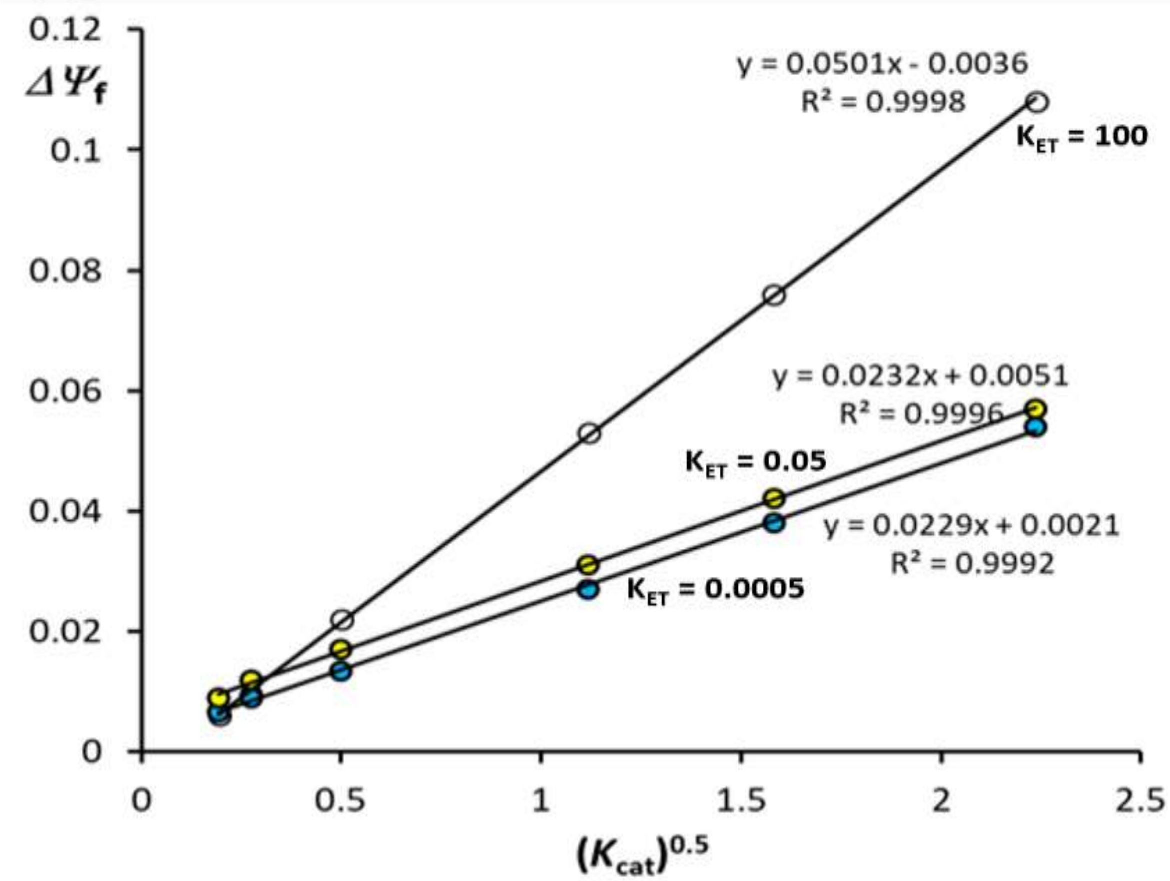
Ket = 100---very fast
dE = 10 mV
Tau = 0.05

$$\Delta\Psi_p := \Psi_p - \Psi_{p-1}$$

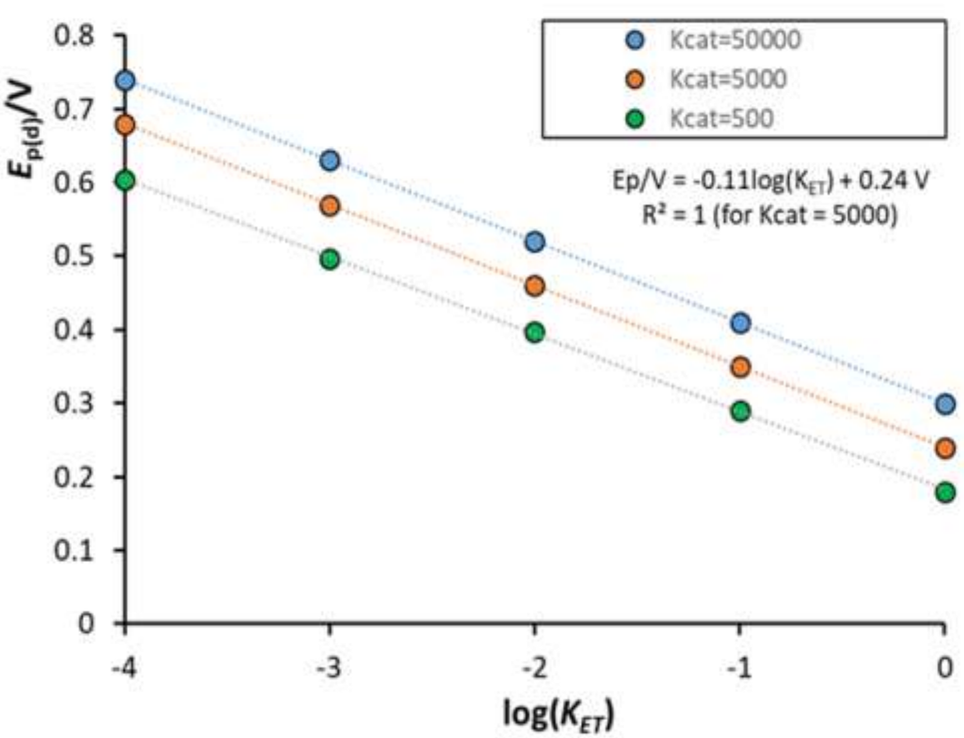
Kcat = 0.038 (a); 0,25 (b); 1.25 (c); 2.5 (d); 5 (e)



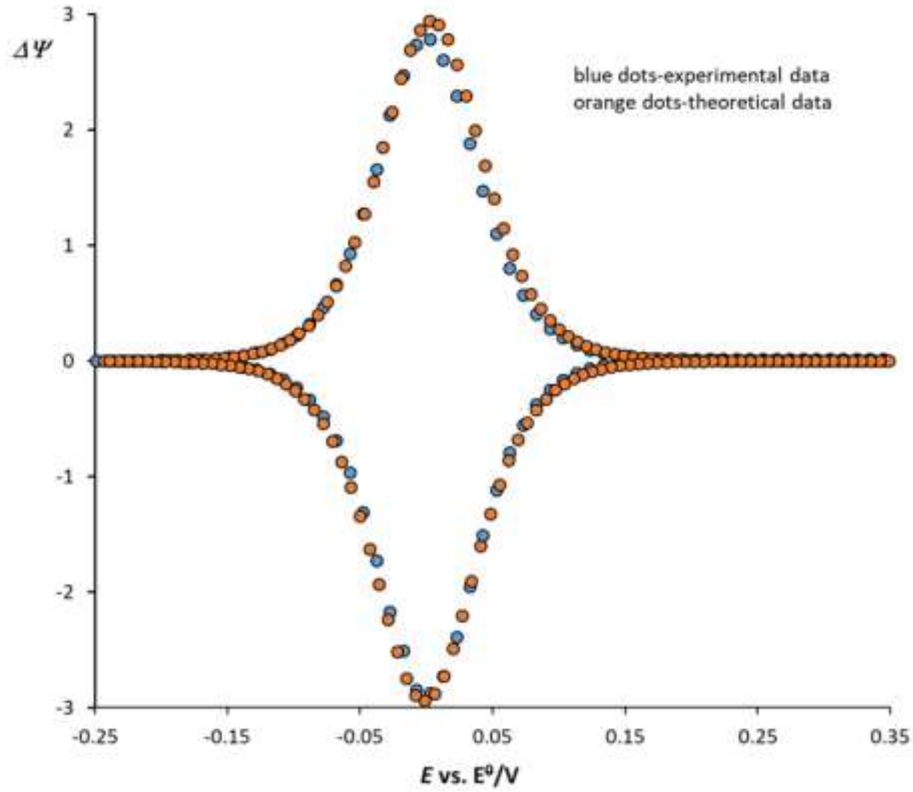




0.12
ΔΨf
0.1
0.08
0.06
0.04
0.02
0
0
0.5
1
1.5
2
2.5
(Kcat)0.5
y = 0.0501x - 0.0036
R² = 0.9998
KET = 100
y = 0.0232x + 0.0051
R² = 0.9996
KET = 0.05
y = 0.0229x + 0.0021
R² = 0.9992
KET = 0.0005



Ep(d)/V
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-4
-3
-2
-1
0
log(KET)
Kcat=50000
Kcat=5000
Kcat=500
Ep/V = -0.11log(KET) + 0.24 V
R² = 1 (for Kcat = 5000)



dE = 0.007 V
Tau = 0.7
Scan rate = 10 mV/s
Kcat = 4200 (for theoretical curve)
Ket = 38 (for theoret. curve)
alpha = 0.5
Experimental curve Is oxidation of $K_4[Fe(CN)_6]$
In pH of 2,
in presence of Vit. C
Experimental Kcat is 7000 M-1s-1 at graphene.

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