Теоретска анализа на иреверзибилна инактивација на почетната редокс активна форма во техниката протеин-филм волтаметрија

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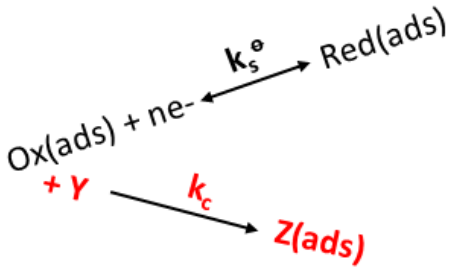
Abstract

При физиолошки услови, редокс протеините и ензимите често подложат на процеси на неповратна инактивација. Во ова истражување, волтаметријата на протеински филм со квадратно-бранова волтаметрија е применета за да се анализираат електрохемиските карактеристики на липофилните редокс протеини и ензими. Во теоретскиот модел за овој механизам, почетната редокс форма на даденият редокс ензим истовремено учествува и во електрохемиска трансформација на површината од работната електрода и во неповратна хемиска реакција на инактивација. Студијата нуди детална табелација која издвојува карактеристични волтамограми, помагајќи притоа на читателите да го идентификуваат овој електроден механизам и да го разликуваат од феноменот на губитокот на филмот во волтаметријата на протеински филм. Покрај тоа, предложени се неколку соодветни пристапи за определување на кинетиката на двата процеси вклучени во електрохемискиот механизам. Овие наоди се наменети да им помогнат на експериментаторите во областа на волтаметријата на протеински филм (PFV) во точно дефинирање на разгледуваниот електроден механизам.

athematical model

Со Scheme I е претставен хемискиот механизам според кој е разработен математичкиот теоретски модел:



(I)

Scheme I. Schematic description of the model elaborated in this work

Овој модел може да се претстави со следниот сет на диференцијални равенки:

$$(d\Gamma(Ox)/dt) = -I/(nFS) - k_c\Gamma(Ox) \quad (1)$$

$$(d\Gamma(Red)/dt) = I/(nFS) \quad (2)$$

$$(d\Gamma(Z)/dt) = k_c\Gamma(Ox) \quad (3)$$

The differential equations (1-3) have been solved under following conditions:

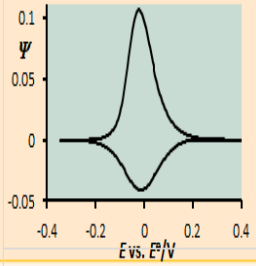
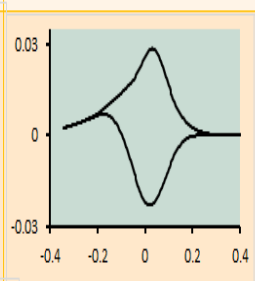
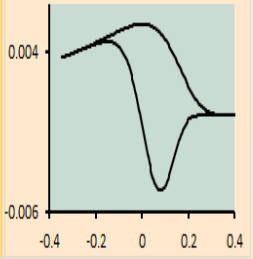
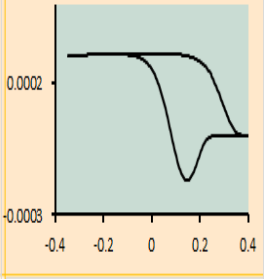
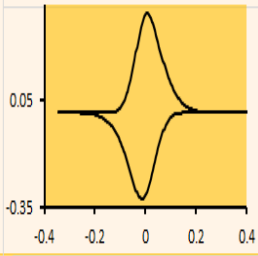
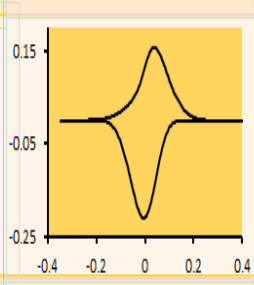
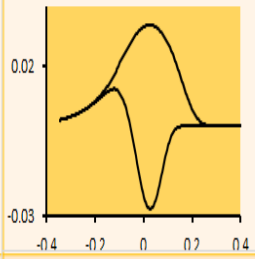
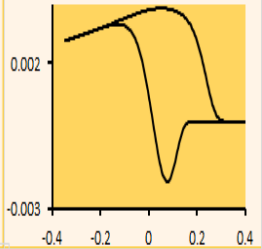
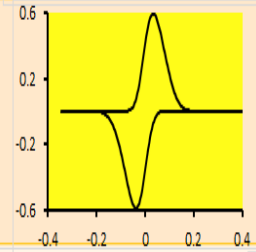
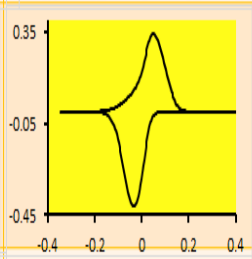
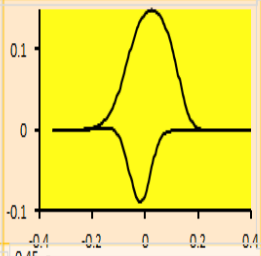
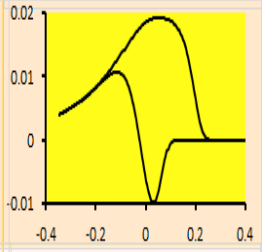
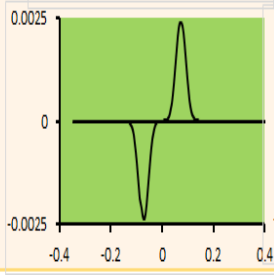
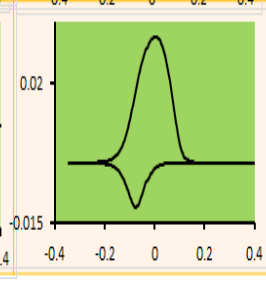
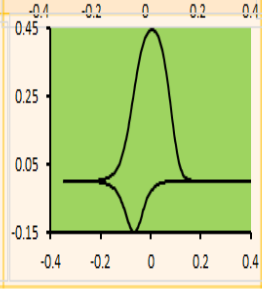
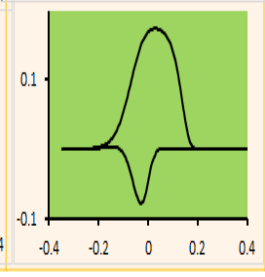
$$t = 0;\ \Gamma(Ox) = \Gamma^*(Ox);\ \ \Gamma(Red) = \Gamma(Z) = 0 \quad (4)$$

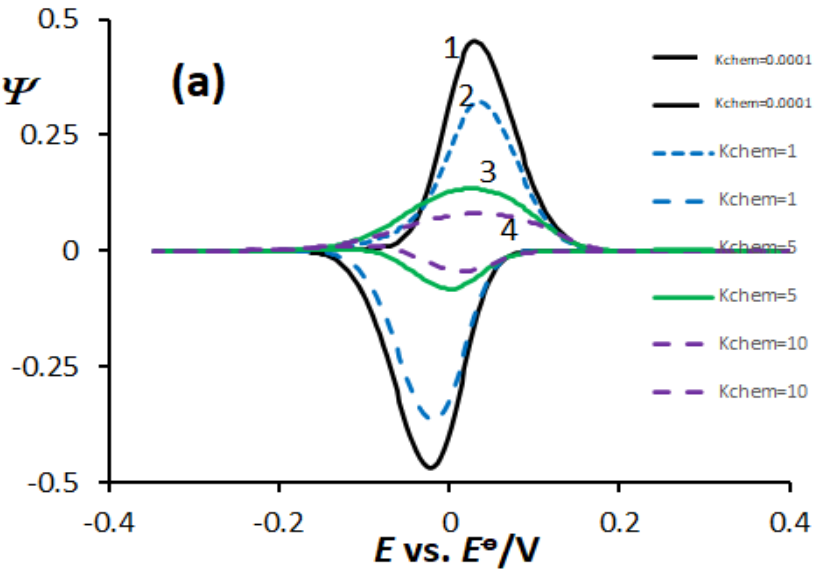
$$t > 0;\ \Gamma(Ox) + \Gamma(Red) + \Gamma(Z) = \Gamma^*(Ox); \quad (5)$$

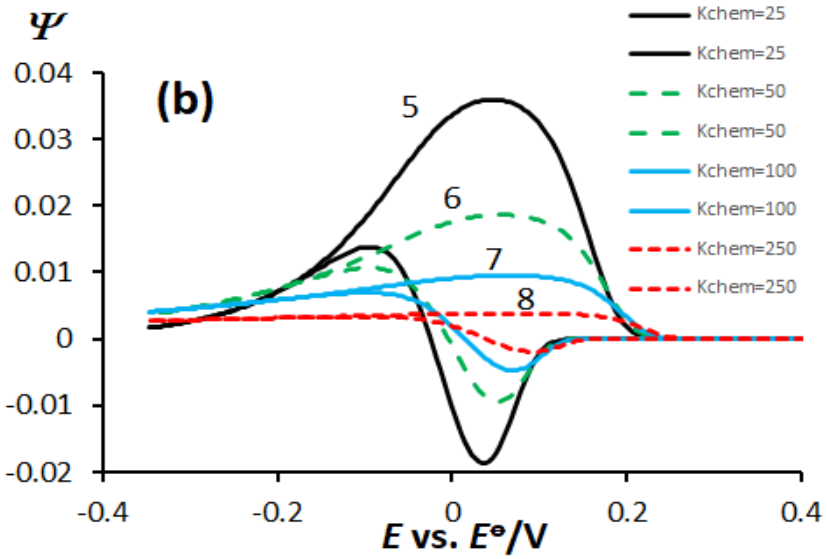
At the working electrode-electrolyte interface, it is assumed that the Butler-Volmer formalism applies (equation 6):

$$(I/nFS) = k_s^e \exp(-\alpha\Phi)\ [\Gamma(Ox) - \exp(\Phi)\ \Gamma(Red)] \quad (6)$$

Table 2. Reduction (forward) and reoxidation (backward) components of the square-wave voltammetric patterns simulated at different rates of electron transfer step and at different kinetics of irreversible chemical reaction.

K_{ET} \ K_{chem}	< 0.05	1	5	50
0.03				
0.2				
1				
10				


(a)
Ψ
0.5
0.25
0
-0.25
-0.5
-0.4
-0.2
0
0.2
0.4
E vs. E⁰/V
1
2
3
4
Kchem=0.0001
Kchem=0.0001
Kchem=1
Kchem=1
Kchem=5
Kchem=5
Kchem=10
Kchem=10


(b)
Ψ
0.04
0.03
0.02
0.01
0
-0.01
-0.02
-0.4
-0.2
0
0.2
0.4
E vs. E⁰/V
5
6
7
8
Kchem=25
Kchem=25
Kchem=50
Kchem=50
Kchem=100
Kchem=100
Kchem=250
Kchem=250

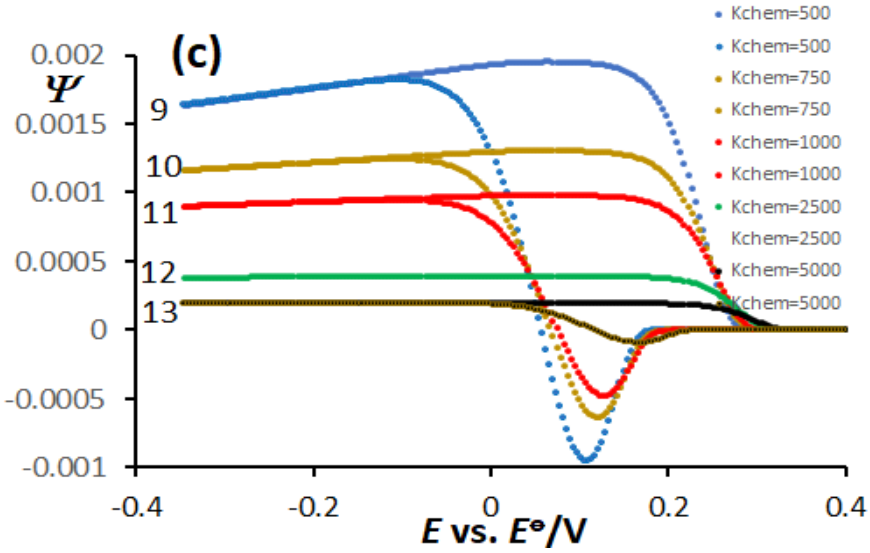
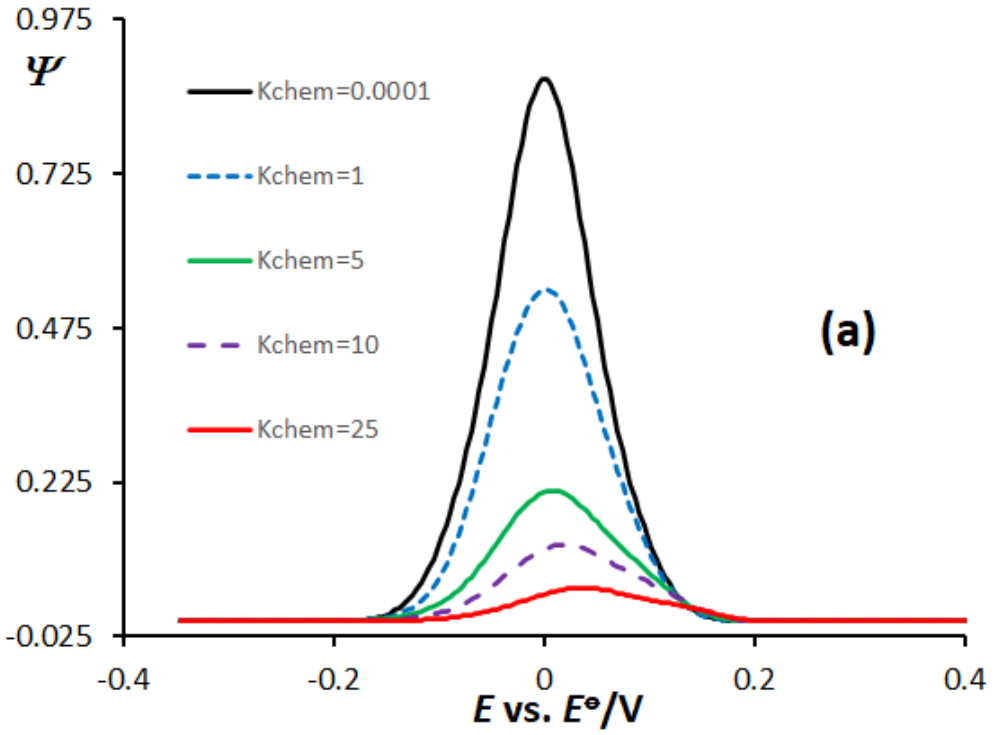

(c)
Ψ
0.002
0.0015
0.001
0.0005
0
-0.0005
-0.001
-0.4
-0.2
0
0.2
0.4
E vs. E⁰/V
9
10
11
12
13
Kchem=500
Kchem=500
Kchem=750
Kchem=750
Kchem=1000
Kchem=1000
Kchem=2500
Kchem=2500
Kchem=5000
Kchem=5000

Figure 1



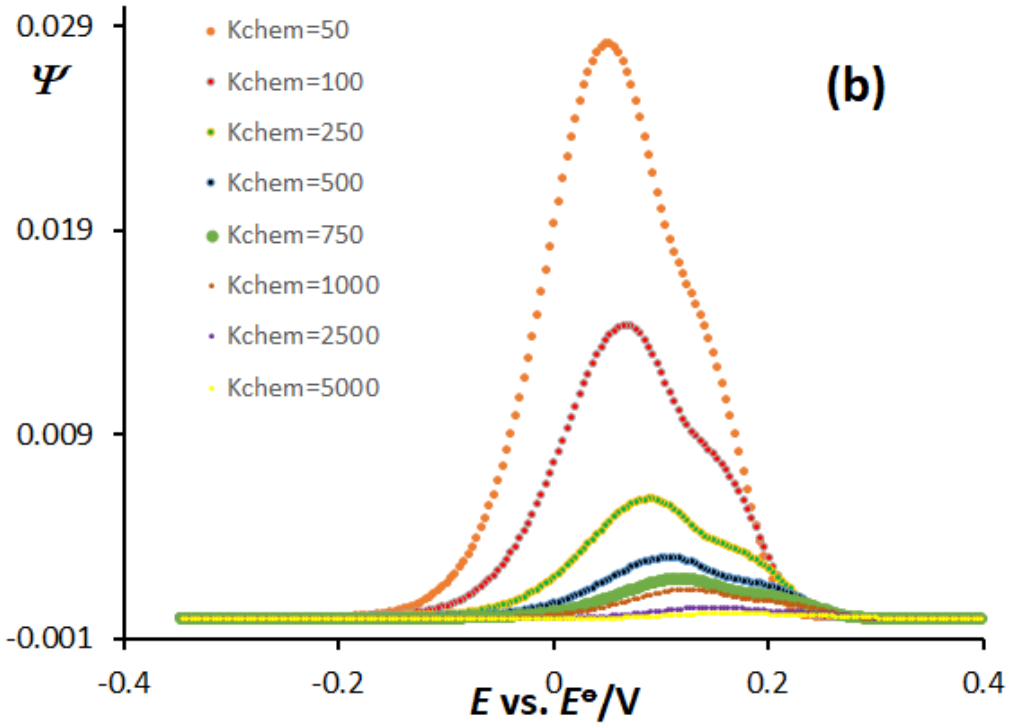


Figure 2

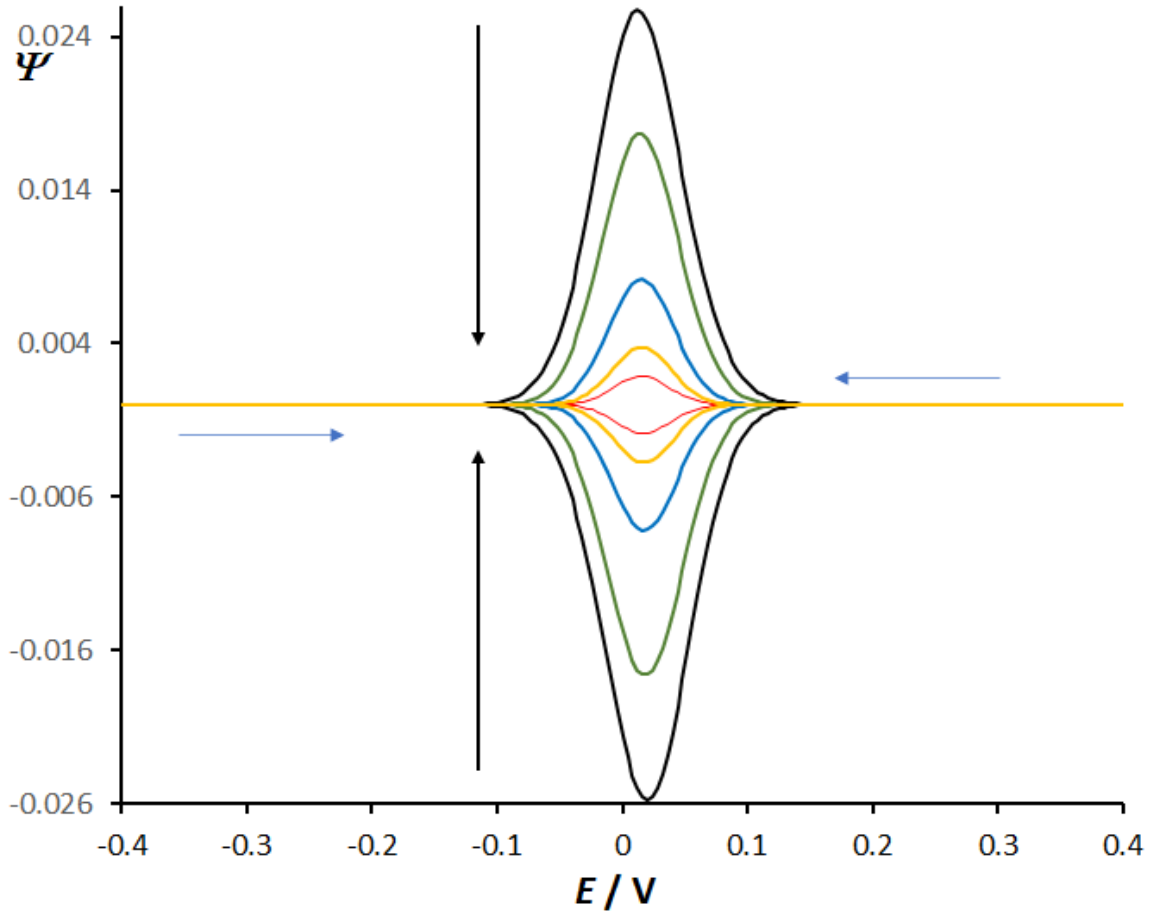


Figure 3.

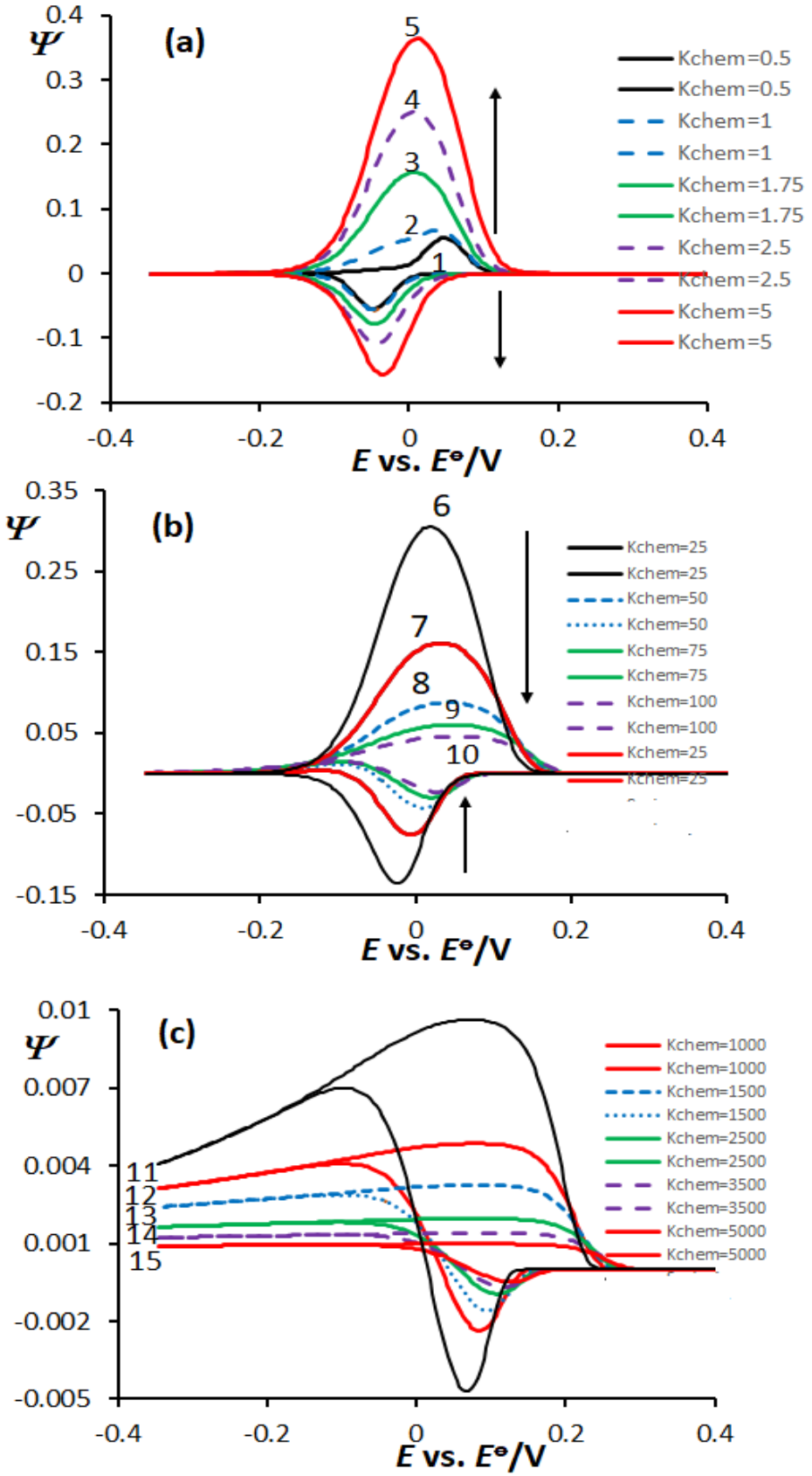

(a)
Ψ
E vs. E°/V
Kchem=0.5
Kchem=0.5
Kchem=1
Kchem=1
Kchem=1.75
Kchem=1.75
Kchem=2.5
Kchem=2.5
Kchem=5
Kchem=5
(b)
Kchem=25
Kchem=25
Kchem=50
Kchem=50
Kchem=75
Kchem=75
Kchem=100
Kchem=100
Kchem=25
(c)
Kchem=1000
Kchem=1000
Kchem=1500
Kchem=1500
Kchem=2500
Kchem=2500
Kchem=3500
Kchem=3500
Kchem=5000
Kchem=5000

Figure 4

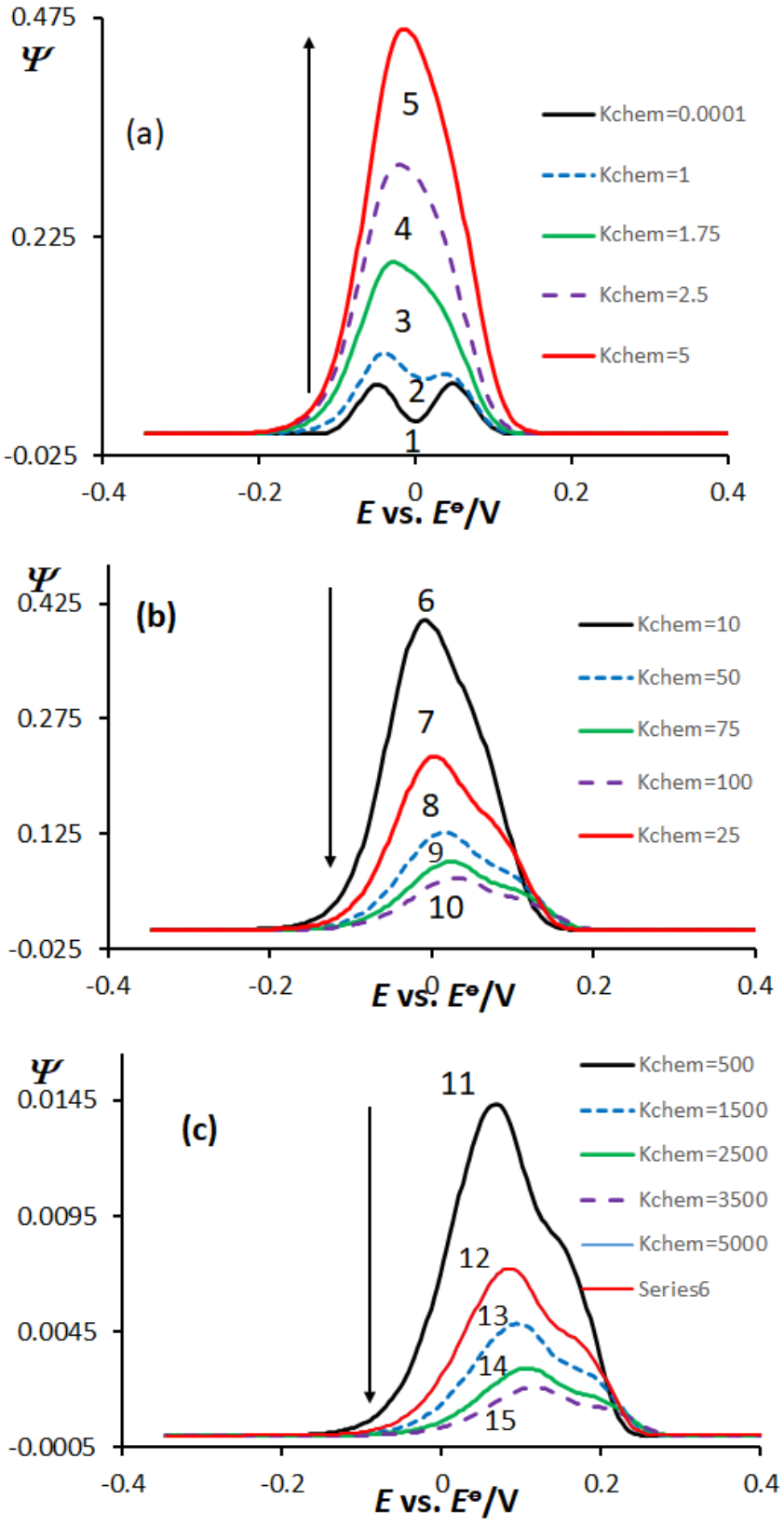

0.475
Ψ
(a)
0.225
-0.025
5
4
3
2
1
Kchem=0.0001
Kchem=1
Kchem=1.75
Kchem=2.5
Kchem=5
-0.4
-0.2
0
0.2
0.4
E vs. E°/V
Ψ
0.425
(b)
0.275
0.125
-0.025
6
7
8
9
10
Kchem=10
Kchem=50
Kchem=75
Kchem=100
Kchem=25
-0.4
-0.2
0
0.2
0.4
E vs. E°/V
Ψ
0.0145
(c)
0.0095
0.0045
-0.0005
11
12
13
14
15
Kchem=500
Kchem=1500
Kchem=2500
Kchem=3500
Kchem=5000
Series6
-0.4
-0.2
0
0.2
0.4
E vs. E°/V

Figure 5

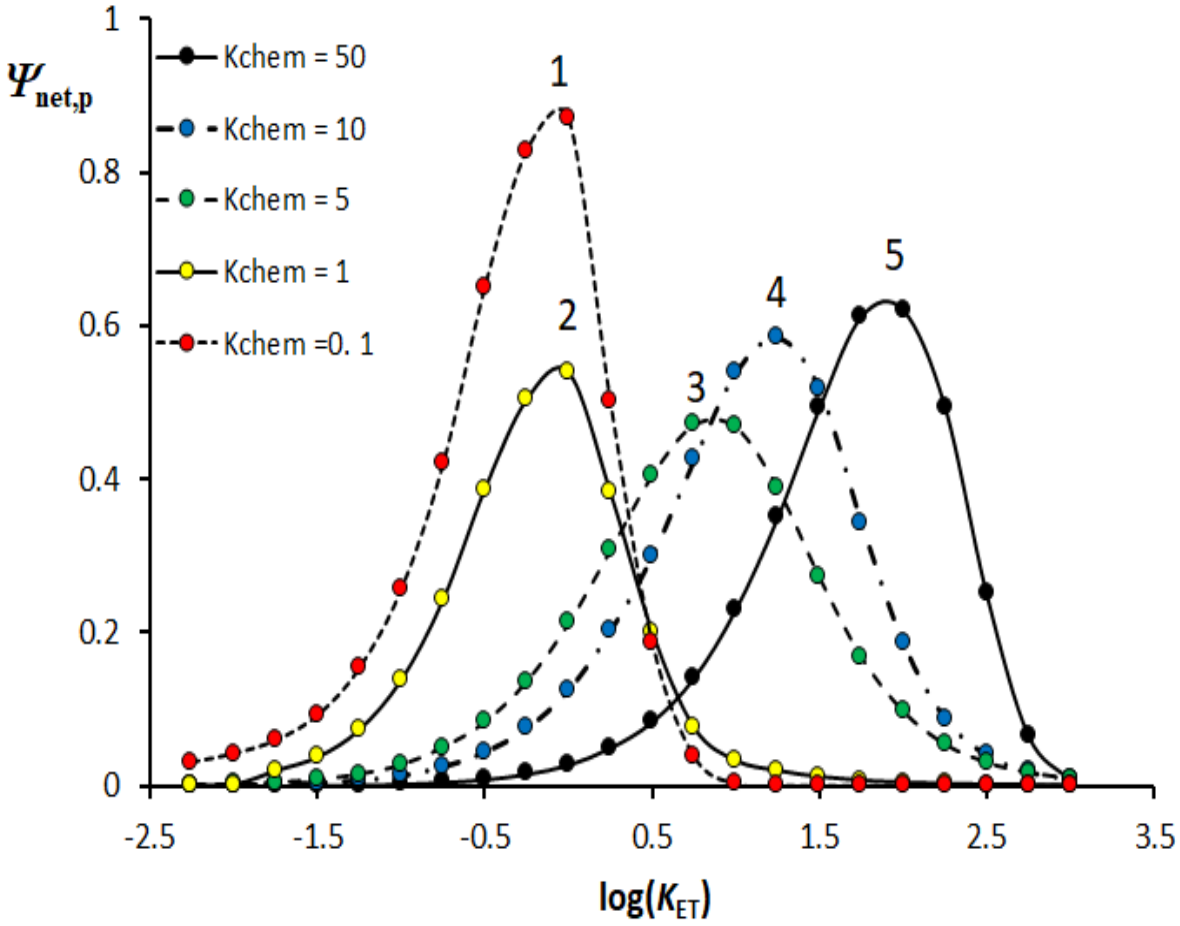

$\Psi_{net,p}$
Kchem = 50
Kchem = 10
Kchem = 5
Kchem = 1
Kchem =0. 1
1
2
3
4
5
1
0.8
0.6
0.4
0.2
0
-2.5
-1.5
-0.5
0.5
1.5
2.5
3.5
log(K_{ET})

Figure 6

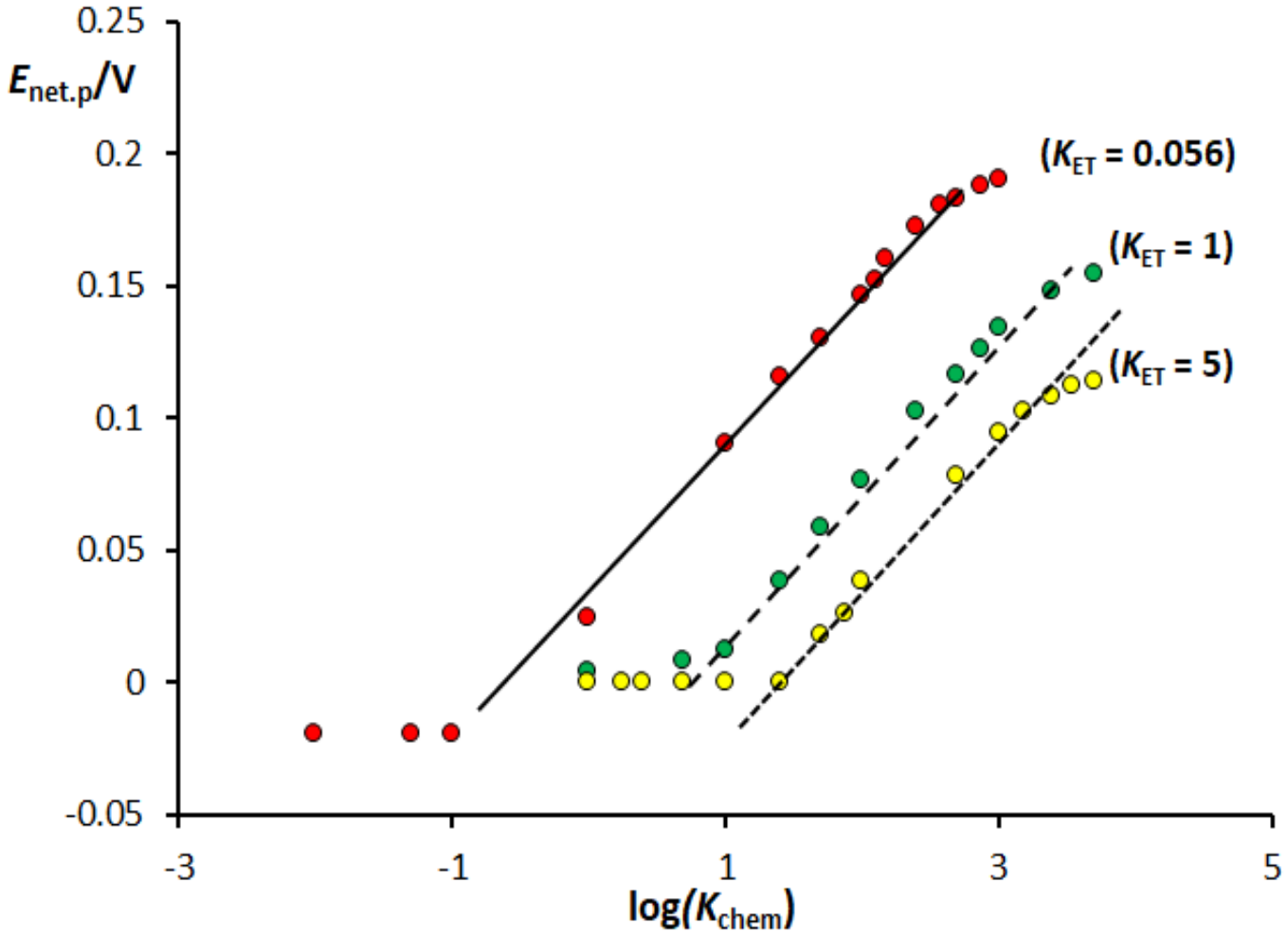

0.25
$E_{net.p}$/V
0.2
0.15
0.1
0.05
0
-0.05
-3
-1
1
3
5
log(K_{chem})
(K_{ET} = 0.056)
(K_{ET} = 1)
(K_{ET} = 5)

Figure 7

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