A Novel Dimensionless Parameter for Predicting Peak Currents in Square-Wave Voltammetry

Rubin Gulaboski

Faculty of Medical Sciences, Goce Delcev University, Stip, Macedonia

Abstract

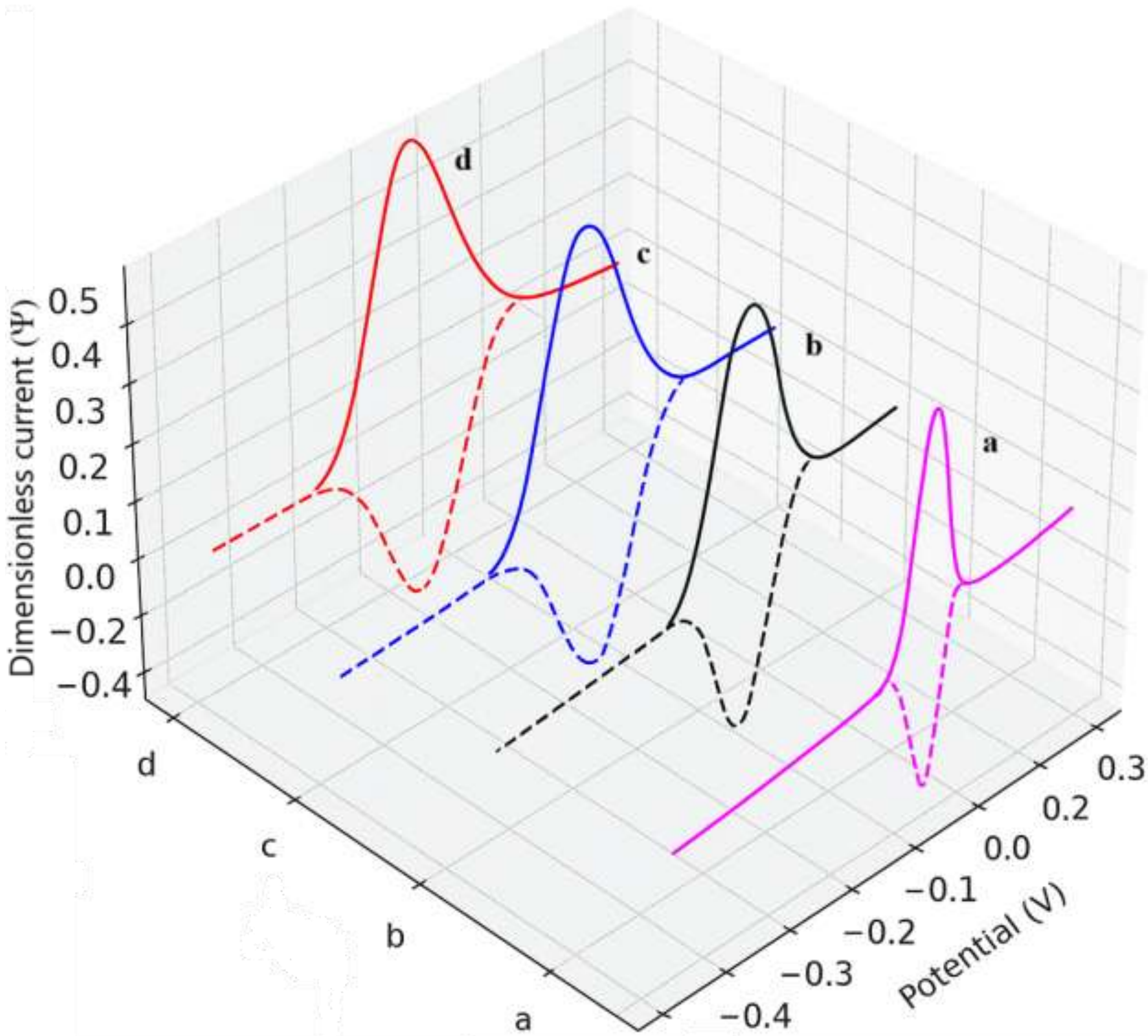
Square-wave voltammetry (SWV) is most advanced electroanalytical technique widely employed for probing redox processes owing to its superior resolution and signal-to-noise characteristics. Despite its advantages, a fundamental theoretical limitation persists, i.e., the absence of a unified formalism capable of accurately describing peak current behavior under a broad spectrum of kinetic and experimental conditions. In contrast to linear scan voltammetry, where the Randles–Ševčík equation provides a direct and well-established relationship between peak current and system parameters, SWV introduces inherently complex, time-dependent perturbations of interfacial concentration gradients due to its pulsed excitation protocol. These perturbations, compounded by the interplay of square-wave amplitude, potential step, temperature, diffusion coefficient, and electron-transfer kinetics, have hindered the derivation of a general analytical expression governing peak current magnitudes in SWV.

In the present study, we conducted comprehensive theoretical simulations of a simple one-electron redox system: **Red ⇌ Ox + e-** modeled under the Butler-Volmer formalism, accounting for diffusion-controlled mass transport. Through this analysis, we introduce a novel dimensionless parameter X defined as:

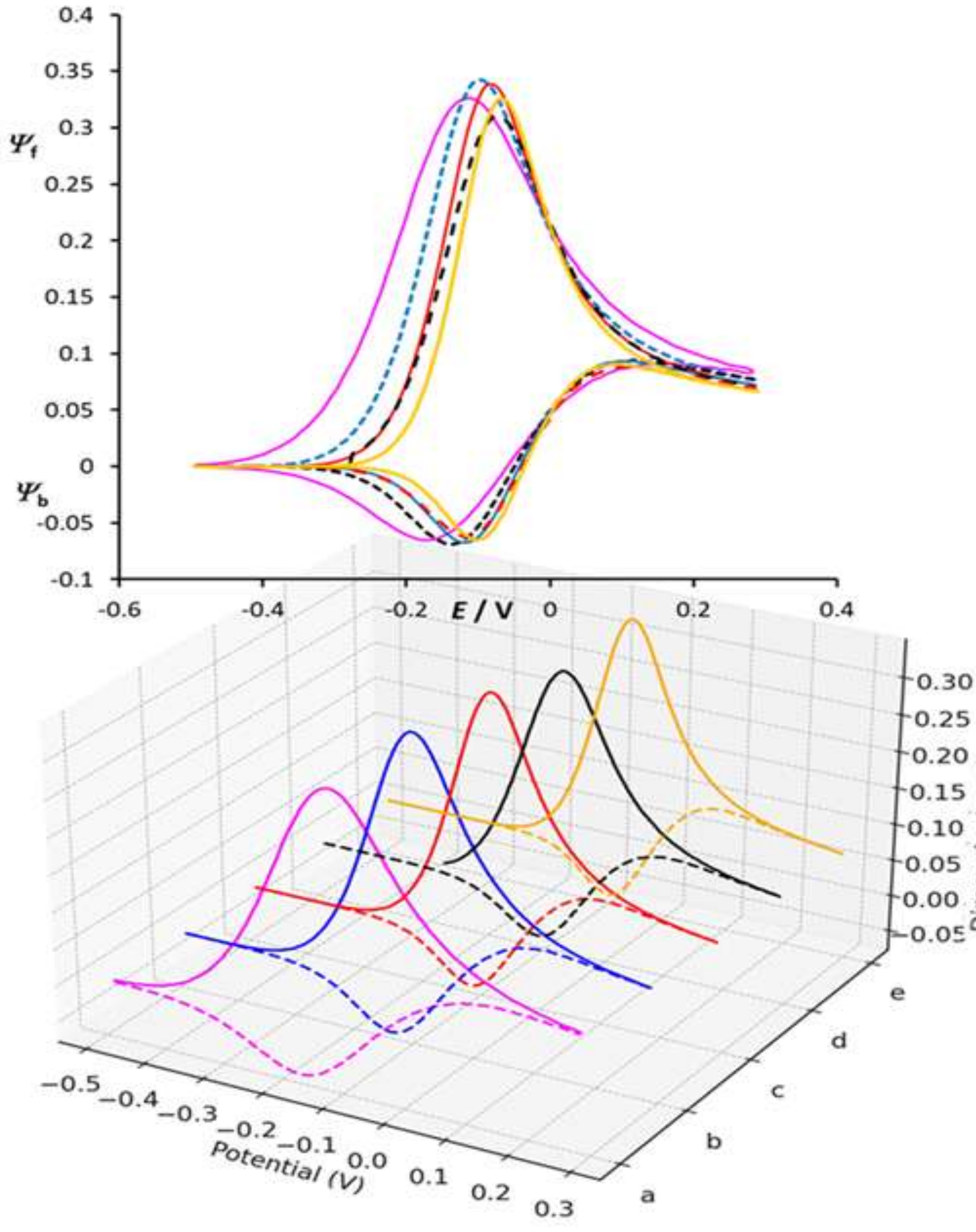
$$X = \text{const.} \times \frac{dE \cdot F}{RT} \cdot \left(\frac{E_{sw}}{dE}\right)^{0.5} \cdot \frac{K}{1+K}$$

which consolidates the contributions of the most critical physical and experimental variables, i.e. temperature (*T*), potential step (*dE*), square-wave amplitude (*Esw*), electron-transfer rate constant (*ks*), frequency (*f*), and diffusion coefficient (*D*) via the dimensionless kinetic parameter *K*. Our preliminary results demonstrate that, when the ratio of square-wave amplitude to potential step is held constant, the peak currents in SW voltammograms remain invariant across wide ranges of temperatures and kinetic regimes, provided that this unified parameter *X* is fixed.

This study therefore reports, for the first time, the identification of a dimensionless descriptor that integrates the multifactorial influences on peak current behavior in SWV. The findings establish a conceptual basis for the development of a generalized theoretical framework for SWV and contribute to a deeper understanding of kinetic redox processes under square-wave perturbation.



d
c
b
a
Dimensionless current (Ψ)
0.5
0.4
0.3
0.2
0.1
0.0
−0.2
−0.4
d
c
b
a
0.3
0.2
0.0
−0.1
−0.2
−0.3
−0.4
Potential (V)



0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
-0.05
-0.1
Ψ_f
Ψ_b
-0.6
-0.4
-0.2
E / V
0
0.2
0.4
0.30
0.25
0.20
0.15
0.10
0.05
0.00
−0.05
Dimensionless Current (Ψ)
a
b
c
d
e
−0.5
−0.4
−0.3
−0.2
−0.1
0.0
0.1
0.2
0.3
Potential (V)

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