

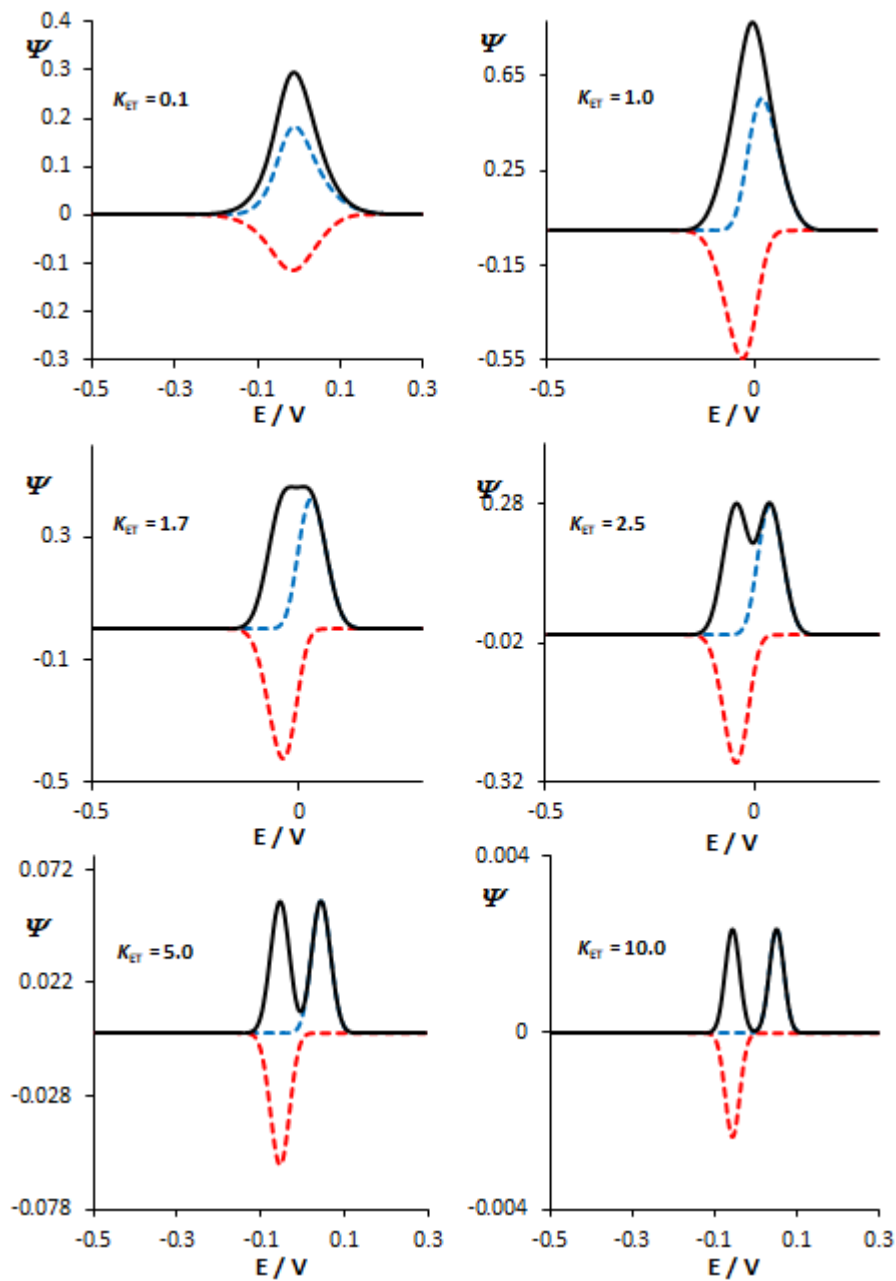
SPLIT PHENOMENON OF NET PEAK IN SQUARE-WAVE VOLTAMMOGRAMS OF ELECTROCHEMICAL MECHANISMS COUPLED WITH CHEMICAL REACTIONS

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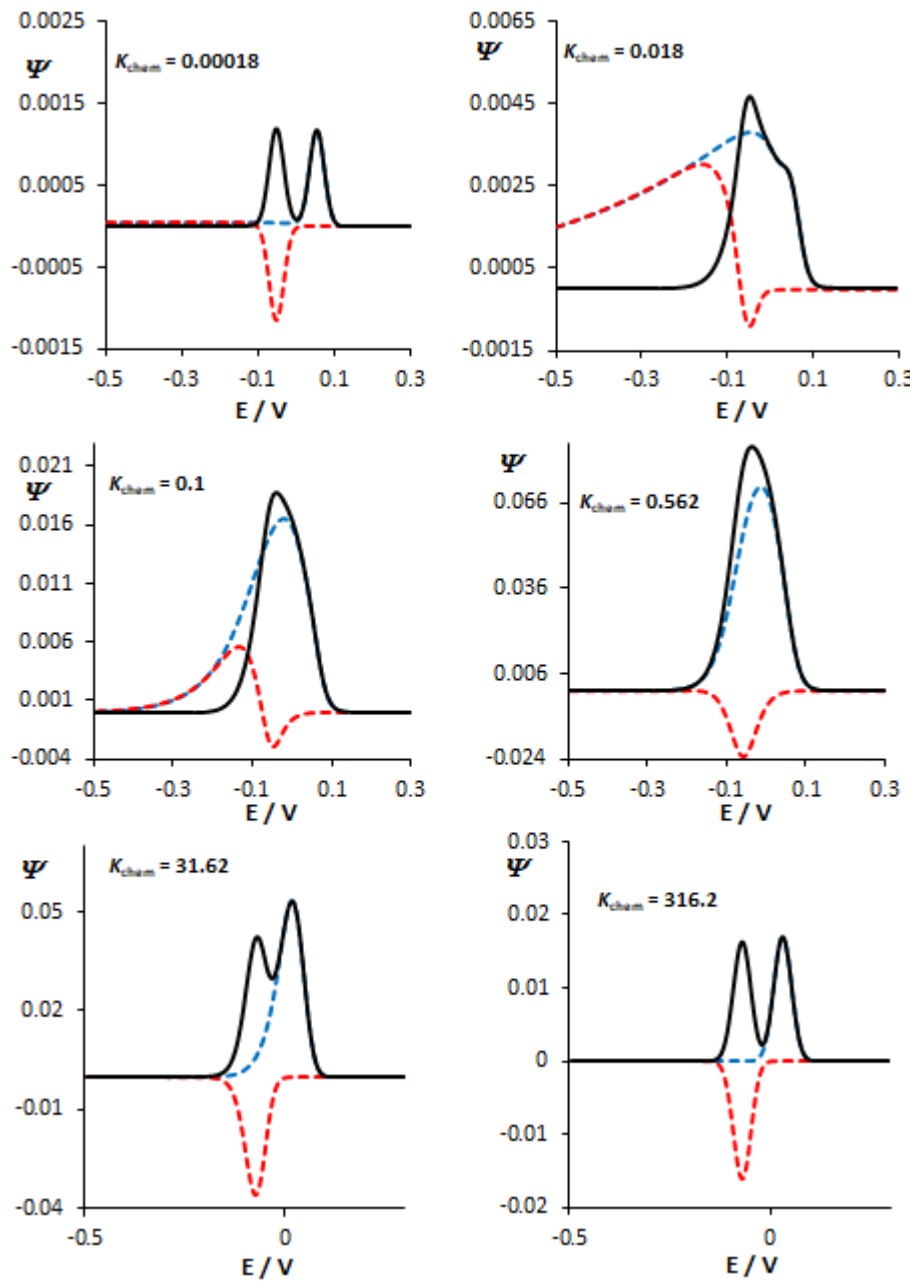
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Abstract

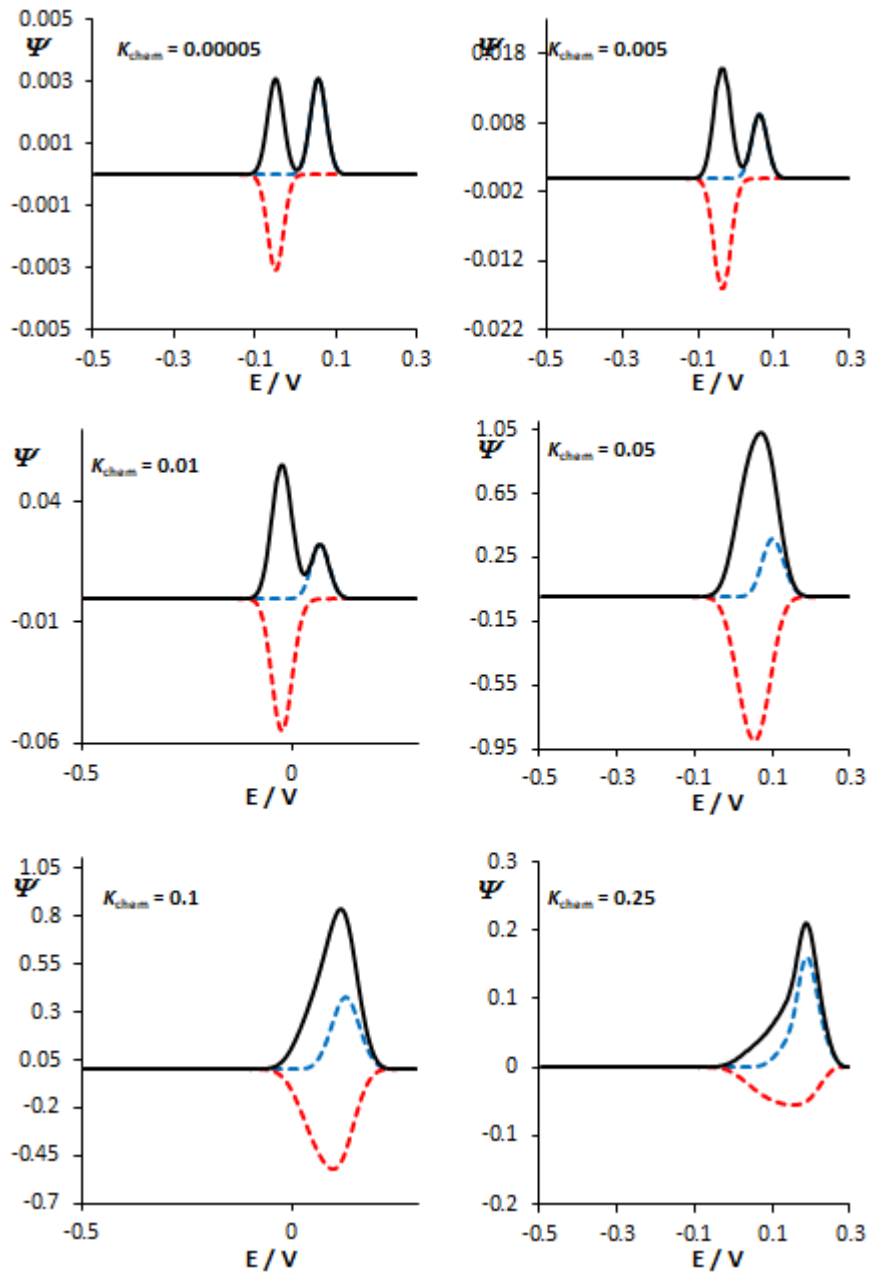
Square Wave Voltammetry (SWV) overlays square wave potential pulse waveforms on a continuously rising staircase ramp. In SWV, the standard current sampling approach is centered on the later part of each applied potential pulse. Here, the influence of the so-called charging currents is effectively reduced, while the Faradaic currents (resulting from electron exchange between the working electrode and the redox system under study) maintain significant magnitude. The currents measured at the end of direct pulses are labeled as "forward" current components. Conversely, currents detected during reverse pulses are denoted as the "reverse" current components, which inherently exhibit an opposite sign to the forward currents, in the square-wave voltammetric displays. In SWV, the net current-voltage curve stems from the variance between the forward and reverse currents. This essentially encapsulates a collective measurement of the magnitude of both current components at every potential level. As documented in many theoretical works, SWV is invaluable for assessing surface-bound redox systems, making it a particularly effective instrument in the realm of protein-film voltammetry. As emphasized in numerous pivotal theoretical studies of our group [1-22], a range of phenomena manifest in SW voltammetric readings. These phenomena correlate with varied electrochemical mechanisms, underpinned by the prominent surface activity of all participants within the electrode process. Notably, attributes like the "quasireversible maximum" and the "splitting of the net SW peak" stand out as defining features of redox systems that exhibit strong surface activity on the working electrode. While both aforementioned phenomena are instrumental in deriving kinetic parameters connected to electron transfer rates via refined methods, the capacity of the "split net SW peak" to differentiate electrochemical mechanisms intertwined with chemical reactions remains under-investigated. In this work, our investigation into the "splitting of net SWV peak" seeks to craft direct diagnostic methods that can segregate surface electrochemical processes tied to diverse chemical reactions.



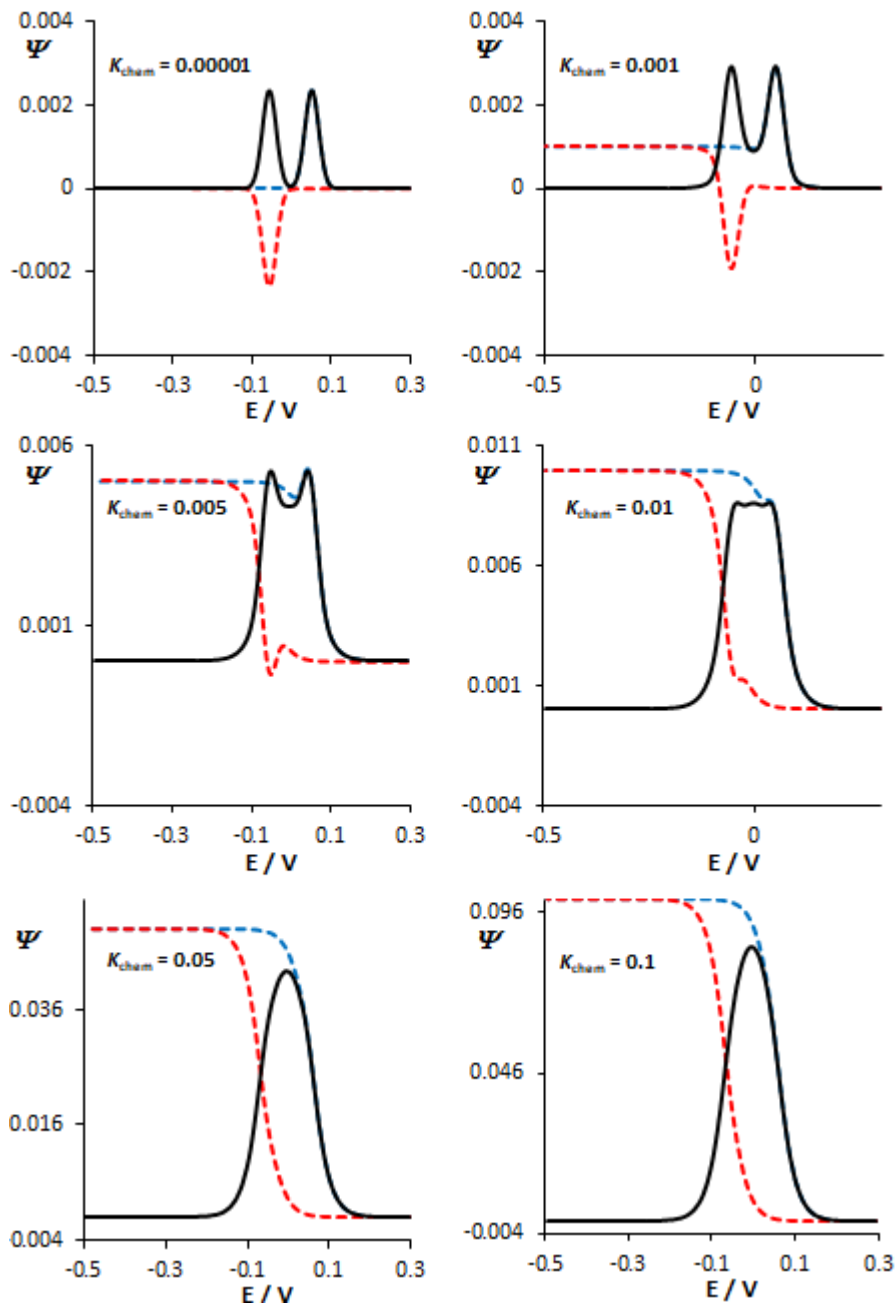
Split Square-Wave Voltammograms of “simple” surface redox systems calculated as a function of dimensionless kinetic parameter of electron transfer step



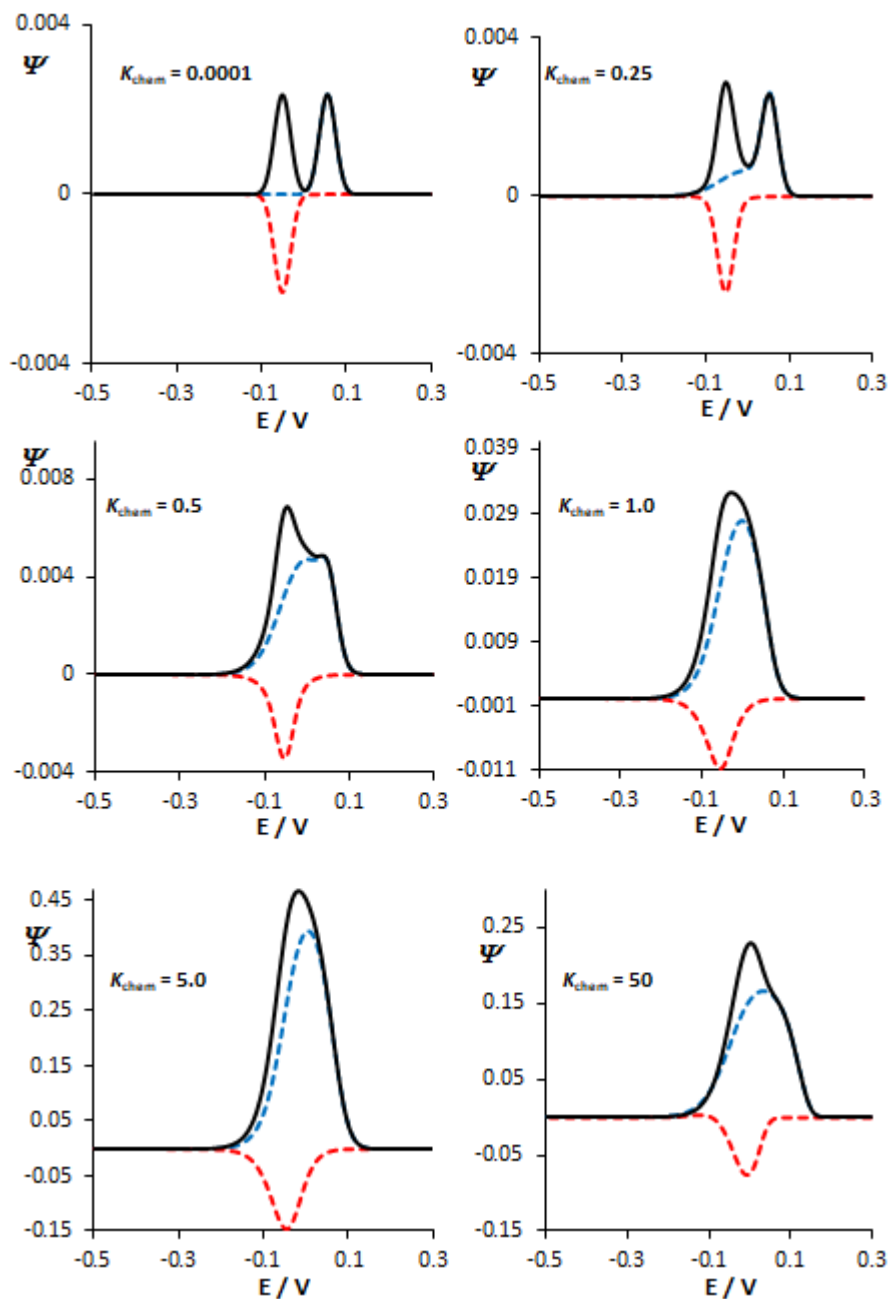
Split Square-Wave Voltammograms of “simple” surface redox systems coupled with preceding chemical step (CE mechanism) calculated as a function of dimensionless chemical kinetic parameter



Split Square-Wave Voltammograms of “simple” surface redox systems coupled with follow up chemical step (surface EC mechanism) calculated as a function of dimensionless chemical kinetic parameter



Split Square-Wave Voltammograms of “simple” surface redox systems coupled with regenerative follow up chemical step (surface EC' mechanism) calculated as a function of dimensionless chemical kinetic parameter



Split Square-Wave Voltammograms of “simple” surface redox systems coupled with parallel chemical step linked to initial redox form, calculated as a function of dimensionless chemical kinetic parameter

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