Linear sweep voltammetry with non-triangular waveforms: New opportunities in electroanalysis

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Abstract

The voltammetry of two simultaneous electrochemically reversible reactions with different formal potentials is investigated at a macroelectrode for a conventional linear potential waveform and a herein newly proposed semi-circular potential waveform, which, at the midpoint of the potential window shows an instantaneous infinite scan rate and relatively very slow scan rates in other areas of the wave. We show that the method increases the sensitivity of detection of individual species by greatly amplifying the peak current of one species while suppressing the interference with the other species and is thus ideal for analytical applications.

1 Introduction

Typical cyclic voltammetry and linear voltammetry employ a linear potential wave¹ in which the scan rate is constant throughout the voltammetric sweep, and is used to extract information such as analyte concentrations, diffusion constants, and rate constants of a redox system.² The potential wave for linear voltammetry is expressed by the following equation:

$$E(t) = \pm \nu t + E(t = 0) \quad (1)$$

where the $\pm$ sign indicates oxidation or reduction and ν is the scan rate. For analytical applications, other techniques such as differential pulse voltammetry (DPV) and square wave voltammetry (SWV) are used because of their sensitivities and their abilities to effectively suppress the capacitive current effect on the voltammogram.³ However, the interpretation of SWV is often more complex compared to cyclic voltammetry.^{1;4;5} We herein propose an alternative method to perform sweep voltammetry for electroanalysis

using a semi-circular potential sweep, which gives an instantaneous infinite scan rate at the midpoint of the potential window. Since the current is proportional to the scan rate, the aforementioned feature greatly increases the current response at the potential at which the infinite scan rate is observed if this coincides with a Faradaic feature in the voltammetry. Additionally, the semi-circular potential sweep applies relatively slow voltage scan rates in other parts of its wave, thereby suppressing the current response in these regions. Our analysis shows that these two features, instantaneous infinite scan rate and relative suppression of current everywhere else, is beneficial in electroanalysis because the peak current of one species can be greatly amplified while the current resulting from other species can be much suppressed.

2 Theory

In the following section, the theoretical model is introduced and the proposed new semi-circular potential waveform is explained. Additionally, we introduce the dimensionless coordinates employed in the simulation.

2.1 Theoretical model

We investigate two simple one-electron electrochemically-reversible reduction reactions of A to C and B to D simultaneously at a planar macroelectrode under diffusion-only conditions, where species A and C have equal diffusion coefficients as do species B and D , but the redox couples A/C and B/D may have different diffusion coefficients from each other:

The system of interest is simulated under the assumption that sufficiently high concentration of supporting electrolyte is present in order to suppress migration^{6;7} and ensure diffusion as the only means of mass transport of the analyte to the electrode surface.⁸⁻¹⁰ Although it is noted that when the scan duration time is long, convection¹¹ may need to be taken into consideration.¹²⁻¹⁵ The transport of analytes is described via the one-dimensional diffusion equation given by Fick's second law:^{16;17}

$$\frac{\partial c_j}{\partial t} = D_j \frac{\partial^2 c_j}{\partial x^2} \quad (4)$$

where j is the species under study and D_j is its diffusion coefficient. For the reactions shown in Equation (2) and (3), $D_A = D_C$ and $D_B = D_D$ but $D_A \neq D_B$. Since the two reactions are independent of each other, we can establish boundary conditions akin to that of a one-species reaction where it is assumed that initially only the reactant is present in the bulk solution^{1;16} and prior to applying potential, the concentration of the reactant and product are uniform in space:^{2;18}

$$t \leq 0, \text{ all } x, c_A = c_A^*, c_C = 0 \quad (5)$$

$$t \leq 0, \text{ all } x, c_B = c_B^*, c_D = 0 \quad (6)$$

As t increases, c_A , c_B , c_C , and c_D near the electrode surface vary but no change is observed at the outer boundary surface:

$$t > 0, x \rightarrow \infty, c_A = c_A^*, c_C = 0 \quad (7)$$

$$t > 0, x \rightarrow \infty, c_B = c_B^*, c_D = 0 \quad (8)$$

Due to conservation of mass, the amount of A and B consumed at the electrode surface equal the amount of C and D produced, giving the conditions:

$$t > 0, x = 0, -\frac{\partial c_A}{\partial x} = \frac{\partial c_C}{\partial x} \quad (9)$$

$$t > 0, x = 0, -\frac{\partial c_B}{\partial x} = \frac{\partial c_D}{\partial x} \quad (10)$$

assuming $D_A = D_C$ and $D_B = D_D$. Therefore for the diffusion coefficients established above, the following conditions hold true for all space and time:

$$c_A + c_C = c_A^* \quad (11)$$

$$c_B + c_D = c_B^* \quad (12)$$

The electrode kinetics can be described via the Butler-Volmer equation for a general one-electron reaction of $O + e \rightleftharpoons R$ where $O = A$ or B and $R = C$ or D , given as:¹⁹⁻²¹

$$j = k^0 \exp \left[\frac{-\alpha_{O/R} F (E - E_{f,O/R}^0)}{RT} \right] [O]_0 - k^0 \exp \left[\frac{(1 - \alpha_{O/R}) F (E - E_{f,O/R}^0)}{RT} \right] [R]_0 \quad (13)$$

where j is the flux of the reactant to the electrode surface, k^0 is the standard electrochemical rate constant, $[O]_0$ and $[R]_0$ are the surface concentrations of the reactant and product, respectively. α is the transfer coefficient,^{22;23} F , R , and T have their usual meanings, E is the applied potential and $E_{f,O/R}^0$ is the formal potential of the redox couple under investigation. Butler-Volmer is flexible and can be applied generally and thus we have implemented a Butler-Volmer boundary condition, shown in Equation (13), with a large k^0 for the electrode surface. The flux of the species to the electrode surface is described via Fick's first law, which can be written in the form:

$$j = -D_O \left(\frac{\partial c_O(x,t)}{\partial x} \right)_{x=0} = -[k_{red} c_O(0,t) - k_{ox} c_R(0,t)] \quad (14)$$

assuming equal diffusion coefficients for O and R . Using the relationships $\theta = \frac{F}{RT} (E - E_{f,O/R}^0)$, $k_{red} = k^0 e^{-\alpha\theta}$, and $k_{ox} = k^0 e^{(1-\alpha)\theta}$, Equation (14) can be written as:

$$D_O \left(\frac{\partial c_O(x,t)}{\partial x} \right) = k^0 e^{-\alpha\theta} c_O(0,t) - k^0 e^{(1-\alpha)\theta} c_R(0,t) \quad (15)$$

Equation (14) and (15) give the concentration gradient of the reactant at the electrode surface. In the following, the two systems of interest, the A/C and B/D redox couple, are both assumed to be fully reversible in which the electrode kinetics are fast compared to the mass transport and attain Nernstian equilibrium^{1;24}, thus the boundary condition in Equation (13) can be replaced by:^{4;16}

$$E = E_f^0 + \frac{RT}{F} \ln \frac{[O]_0}{[R]_0} \quad (16)$$

where E is the applied potential. The Nernst equation is used for systems with fast electrode kinetics whereas the Butler-Volmer equation encompasses systems with both, fast and slow electrode kinetics. Our two systems, the A/C and B/D redox couple, are electrochemically reversible and can thus be described with the Nernst equation.

2.2 Dimensionless coordinates

The simulations were run using the dimensionless forms of the expressions given earlier using the conversion factors listed in the following Table.

Table 1: Dimensionless parameters.¹⁶

Parameter	Normalization
concentration	$C_j = \frac{c_j}{c_A^*}$
diffusion coefficient	$d_j = \frac{D_j}{D_A}$
spatial coordinate	$X = \frac{x}{\epsilon}$
time	$\tau = \frac{D_A t}{\epsilon^2}$
potential	$\theta = \left(\frac{F}{RT}\right) (E - E_{f,A/C}^0)$
scan rate	$\sigma = \left(\frac{\epsilon^2}{D_A}\right) \left(\frac{F}{RT}\right) \nu$
current	$J = \frac{I}{\pi \epsilon F D_A c_A^*}$
rate constant	$K^0 = \frac{k^0 \epsilon}{D}$

Given these expressions, Equation (4) can be written in its dimensionless form:

$$\frac{\partial C_j}{\partial \tau} = d_j \frac{\partial^2 C_j}{\partial X^2} \quad (17)$$

and Equation (14) becomes:

$$\frac{C_{O,1} - C_{O,0}}{h} = \frac{1}{d_j} K_0 f(\theta) \{C_{O,0} - [1 + C_R^* - C_{O,0}] e^\theta\} \quad (18)$$

where $C_{O,1}$ and $C_{O,0}$ correspond to the dimensionless concentrations at $X = 1$ and $X = 0$ respectively, $f(\theta) = e^{-\alpha\theta}$, and $h = X_1 - X_0$ assuming O and R have equal diffusion coefficients.

2.3 Semi-circular potential sweep

The goal of this project is to employ a potential wave with an instantaneous infinite scan rate at some potential and a slow scan rate in other areas of the wave in order to selectively amplify the peak current of one species at its formal potential and suppress the current contribution of others for analytical applications. To this end, we introduce a semi-circular potential wave function which possesses all the desired features. As shown in Figure 1, the triangular(linear) potential wave shows a constant scan rate throughout the duration time but the semi-circular wave when centred at $\theta = 0$ has the highest

instantaneous scan rate at $\theta = 0$ and rapidly decreases as the potential becomes further from zero.

Figure 1: Triangular(linear) and semi-circular potential wave graphs centered at 0 with an amplitude of 1. The triangular potential wave shows a constant scan rate throughout the duration time whereas the semi-circular potential wave shows the highest instantaneous scan rate at $\theta = 0$ but rapidly decreases as the potential becomes further from 0.

The semi-circle function is advantageous in a way that the potential wave displays the desired features and the equation is easily understood. The general form of a circle equation centred at (a, b) is given as:

$$(x - a)^2 + (y - b)^2 = r^2 \quad (19)$$

where a and b determine the shift from the point of origin defined as $(0, 0)$, and r is the radius. Solving Equation (19) for y yields:

$$y = \pm \sqrt{r^2 - (x - a)^2} + b \quad (20)$$

When applying Equation (20) to voltammetry, y represents the function of the potential θ with respect to time τ , r represents the amplitude A , x represents the time τ , a represents the fraction of the maximum time when the centre of each semi-circle is observed, thus defined as $a = c\tau_{max}$. For example in Figure 1, the first semi-circle is centred around $\tau = 0$ and the second semi-circle is centre around $\tau = \tau_{max}$, thus they were plotted using $c = 0$ and $c = 1$ respectively. b represents the potential shift expressed as θ_{shift} , which is defined as $\theta_{shift} = \theta_{avg} - \theta_{f,A/C}^0$ thus giving the equation:

$$\theta(\tau) = \pm \sqrt{A^2 - (\tau - c\tau_{max})^2} + \theta_{shift} \quad (21)$$

We need to ensure the duration time remains unchanged from the triangular potential wave with varied scan rates. For this purpose, we introduce a new parameter:

$$\theta(\tau) = \pm \sqrt{A^2 - [\sigma_{avg} \cdot (\tau - c\tau_{max})]^2} + \theta_{shift} \quad (22)$$

where σ_{avg} represents the average scan rate in dimensionless coordinates and $\tau_{max} = \frac{2A}{\sigma_{avg}}$.

2.4 Simulation via finite differences

All simulations were performed using the finite differences method through discretization of the dimensionless diffusion equation and employing the backward implicit method.^{2;18} The theoretical model introduced above was implemented in *C++* and plotting was done in *Python* with the packages *NumPy* and *matplotlib*. Thorough testing²⁵ was performed via convergence tests, the conservation of mass test, and comparing the peak heights and peak positions with theoretical values.

3 Results and discussion

The results are divided into two sections where (a) we discuss the difference in the voltammetric behavior between the conventional triangular and the newly proposed method for a one species system by shifting the potential window with respect to the formal potential of the *A/C* couple which we have set to $E_{f,A/C}^0 = 0$ and hence $\theta_{f,A/C}^0 = 0$, and (b) we investigate the analytical application of our method by discussing the features of a two species system using the same method. The transfer coefficient, α , is set to a constant value of 0.5 and all results are reported in dimensionless units with $\sigma_{avg} = 10^4$ and $K_0 = 10^{10}$ while changing the θ_{shift} values.

3.1 Single electrochemically reversible species: triangular versus semi-circular potential sweeps

We first focus on one species, *A*, of the *A/C* couple, and compare the results between triangular and semi-circular potential waves as shown in Figure 2. The formal potential of *A/C* is set to 0 and its dimensionless diffusion coefficient, $d_A = d_C$, is 1.0. Figure 2 shows the results at certain θ_{shift} values where 2A corresponds to $\theta_{shift} = -10$, 2B corresponds to $\theta_{shift} = -8$, 2C corresponds to $\theta_{shift} = -4$, 2D corresponds to $\theta_{shift} = 0$, 2E corresponds to $\theta_{shift} = 2$, and 2F corresponds to $\theta_{shift} = 4$. The blue solid line represents the results obtained using the triangular potential wave whereas the green solid line represents results from the semi-circular potential wave. The arrows indicate the direction of the sweep and the dotted line shows the theoretical peak current for the triangular results predicted by the Randles-Ševčík equation^{26;27} for an electrochemically reversible electron transfer given as:^{16;19;28}

$$I_p = -0.446FAc_j^* \sqrt{\frac{FD_j\nu}{RT}} \quad (23)$$

where A is the area of the electrode, c_j^* is the concentration of the species under study, $\frac{F}{RT}$ has its usual meaning, D_j is the diffusion coefficient of the said species, and ν is the scan rate. Equation (23) shows that the peak current has a square root dependence on the scan rate.^{10;29} Equation (23) can then be converted to a dimensionless form using the conversion factors from Table 1, giving

$$J_p = -0.446C_j \sqrt{d_j\sigma} \quad (24)$$

where $C_A = 1.0$.

The peak currents obtained through the triangular potential wave do not show any variance with different θ_{shift} values as predicted, however, those obtained from the semi-circular potential wave show a significant dependence on the θ_{shift} values. Looking at Figure 2A, we do not see much difference between the triangular and semi-circular peak currents, but as θ_{shift} approaches 0, the peak current of the semi-circular potential wave voltammogram increases and at $\theta_{shift} = 0$, where the wave features an infinite scan rate at the formal potential, the peak goes to infinity. In other θ_{shift} values, a sharp peak is also observed. This is due to the singularity of the scan rate that forms in the semi-circular wave function at the midpoint of the potential window as can be seen in Figure 1. When this singularity occurs at the formal potential and in its immediate vicinity of the reduced species, an infinite increase in the peak current is observed and a small but sharp peak is observed at other θ_{shift} values as well. When the θ_{shift} is significantly negative with respect to the formal potential, no sharp peak is observed due to the relatively low sensitivity of the electrochemical reaction kinetics to changes in the applied potential in this potential region.

The fact that the peak current is significantly amplified at the formal potential when $\theta_{shift} = 0$ and suppressed at other θ_{shift} values makes the semi-circular potential sweep a more powerful tool for electroanalysis compared to the conventional triangular wave which shows no peak height variance. The new method can thus be used to selectively detect individual species with different formal potentials and diffusion coefficients that are in a same mixture since the current contribution of one species will be augmented at its formal potential while the current of other species will be minimized, thereby making the interpretation of the results much more obvious and intuitive. Here, we have limited the window of the y-axis in order to better show the difference between the triangular and semi-circular results. A full scale version of Fig.2 and the following figures are provided in the Supporting Information.

Figure 2: Voltammetric scan of species A obtained using triangular and semi-circular potential waves at different θ_{shift} values with a formal potential of 0 and a dimensionless diffusion coefficient of 1.0. A is when $\theta_{shift} = -10$, B is when $\theta_{shift} = -8$, C is when $\theta_{shift} = -4$, D is when $\theta_{shift} = 0$, E is when $\theta_{shift} = 2$, and F is when $\theta_{shift} = 4$. The blue solid line represents the results from the triangular potential wave and the solid green line represents results from the semi-circular potential wave. The dotted line shows the peak current predicted by the Randles-Sevcik equation and the arrows indicate the direction of the sweep.

3.2 Two species triangular versus semi-circular potential sweeps

In the following sections we explore the analytical applications of the semi-circular potential wave by comparing its voltammetric features with that obtained from a triangular potential wave for a two species system containing the A/C couple and B/D couple where both systems are assumed to be electrochemically reversible. We vary the formal potential difference between the two redox couples to study the changes in the voltammetric response of both methods, starting with a formal potential difference of -8 dimensionless units, then -4 , and -2 . In all cases, $d_A = d_C = 1.0$, $d_B = d_D = 0.5$, $C_A = 1.0$, $C_B = 1.0$, and $\theta_{f,A/C}^0 = 0$.

3.2.1 Two species with formal potential difference of -8 dimensionless units

Figure 3 shows the results at the same θ_{shift} values as in Figure 2 but includes the voltammogram for the second species, B . The formal potential difference between the two species is -8 dimensionless units ($\theta_{f,B/D}^0 = \theta_{f,A/C}^0 - 8$), which, in dimensional terms corresponds to approximately -0.21 V at 25 °C. The light blue solid line represents results from the triangular potential wave for species A , the medium dark blue solid line represents results from the triangular potential wave for species B , the dark blue solid line represents the total current of species A and B obtained from the triangular potential wave, the light green solid line represents results from the semi-circular potential wave for species A , the medium dark green solid line represents results from the semi-circular potential wave for species B , and the dark green solid line represents the total current of species A and B obtained from the semi-circular potential wave. The light and dark blue dotted lines show the theoretical peak currents predicted by the dimensionless Randles-Ševčík equation for species A and B , respectively.

If we look at the total current for the triangular potential wave, we see there are two peaks observed, each of which is a result of the contribution of the peak currents of species A and B . Since the individual peak currents do not change with varying θ_{shift} , the two peaks in the total current also remain constant with varying θ_{shift} values. Through simple examination, it is obvious that there are two species in this particular simulation where each species has a different formal potential based on the height of the two peaks and the potential at which they are observed. In addition, for this particular case, one of the peaks of the total current matches the dotted line plotted by the dimensionless Randles-Ševčík equation using the dimensionless diffusion coefficient and concentration for species A . This is due to the fact that the potential at which this peak occurs is the region where species B does not react and thus most of the current contribution comes from species A . In such cases, Randles-Ševčík equation can be used to determine the diffusion coefficient of the current-contributing species. However, this is only applicable

when the formal potential difference between species A and B is significant and the peak current of A is observed at a potential region where minimal or no reaction is observed for species B .

The total current of the semi-circular potential wave also shows there are two species within the same mixture, but significantly amplifies the current contribution of one of the species near its formal potential while suppressing the other, thereby making the analysis much easier. Looking at Figure 3A and 3B, we can see the peak current growing in 3B compared to 3A. It then diminishes in 3C, and increases significantly again in 3D. The subsequent figures 3E and 3F show a gradual decrease in the total peak current. Through simple observation we can determine that the formal potential of A/C and B/D couple must be very close to 0 and -8 dimensionless units, respectively.

Figure 3: Voltammetric scan obtained using triangular and semi-circular potential waves at different θ_{shift} values for species A and B with a formal potential difference of -8 dimensionless units, which, in dimensional terms corresponds to roughly $-0.21V$. The formal potential of A is again 0 , and $d_A = 1.0$ while $d_B = 0.5$. A is when $\theta_{shift} = -10$, B is when $\theta_{shift} = -8$, C is when $\theta_{shift} = -4$, D is when $\theta_{shift} = 0$, E is when $\theta_{shift} = 2$, and F is when $\theta_{shift} = 4$. The light blue solid line represents the results from the triangular potential wave for species A , the medium dark blue solid line represents the results from the triangular potential wave for species B , the dark blue solid line represents the total current of species A and B obtained from the triangular potential wave, the light green solid line represents results from the semi-circular potential wave for species A , the medium dark green solid line represents the results from the semi-circular potential wave for species B , and the dark green solid line represents the total current of species A and B obtained from the semi-circular potential wave. The light and dark blue dotted lines show the peak currents predicted by the Randles-Ševčík equation for species A and B , respectively.

From the trend found in Figure 3, we can expect the semi-circular total current to show two potentials in which an absolute maximum peak height is observed with varying θ_{shift} values, and indeed this is the case as shown in Figure 4. Figure 4 shows the peak heights plotted against the corresponding θ_{shift} values at which they are observed. The light orange dots represent peak heights for species *A*, dark orange dots represent the peak heights for species *B*, and dark red dots represent the peak heights of the total current. The plot for the total current shows that near $\theta_{shift} = 0$ and $\theta_{shift} = -8$, a maximum is observed and these two values correspond to the formal potential of species *A* and *B*, respectively. Therefore Figure 3 and 4 can be used to selectively detect individual species in a mixture and estimate their formal potentials.

Figure 4: Peak height plotted against the corresponding θ_{shift} value at which it is observed for species *A*, *B*, and their total currents obtained through the semi-circular potential wave. The formal potential difference between the two species is -8 dimensionless units, and $d_A = 1.0$ and $d_B = 0.5$. The light orange dots represent the peak heights for species *A*, dark orange dots represent the peak heights for species *B*, and dark red dots represent the peak heights of the total current.

From the above analysis, it is clear that a semi-circular potential wave is a powerful tool for analyzing mixtures, however, Figure 3 shows that when the formal potential difference between two species is significant, the conventional triangular potential wave is sensitive enough to detect them since two distinct peaks are observed in the total current. Therefore we next investigate the limit of detection of the semi-circular potential wave and decrease the formal potential difference between species *A* and *B*.

3.2.2 Two species with formal potential difference of -4 dimensionless units

Figure 5 again shows the voltammetric results of species *A* and *B* with a formal potential difference of -4 dimensionless units ($\theta_{f,B/D}^0 = \theta_{f,A/C}^0 - 4$), which, in dimensional coordinates corresponds to approximately -0.1 V. The results were obtained using both, triangular and semi-circular potential waves. Each figure uses the same color scheme as in Figure 3, however, the results are reported at different θ_{shift} values to better show the results at a θ_{shift} value near the formal potential of each

species. Figure 5A corresponds to $\theta_{shift} = -6$, 5B corresponds to $\theta_{shift} = -4$, 5C corresponds to $\theta_{shift} = -2$, 5D corresponds to $\theta_{shift} = 0$, 5 corresponds to $\theta_{shift} = 2$, and 5 corresponds to $\theta_{shift} = 4$.

The two peaks of the triangular total current that were clearly separate in Figure 3 are merged in Figure 5 and the current contributions from species A and B or their diffusion coefficients cannot be distinguished. On the other hand, the results from semi-circular potential wave again show an infinite increase in the peak current around the formal potential of each species (for a full-size figure, please refer to the Supporting Information), indicating that this new method can be used for sensitive detection when the triangular potential wave cannot.

Figure 5: Voltammetric scan obtained using triangular and semi-circular potential waves at different θ_{shift} values for species A and B with a formal potential difference of -4 dimensionless units, which, in dimensional term corresponds to roughly $-0.1V$. Formal potential of species A = 0, $d_A = 1.0$, and $d_B = 0.5$. A is when $\theta_{shift} = -6$, B is when $\theta_{shift} = -4$, C is when $\theta_{shift} = -2$, D is when $\theta_{shift} = 0$, E is when $\theta_{shift} = 2$, and F is when $\theta_{shift} = 4$. The light blue solid line represents the results from the triangular potential wave for species A, the medium dark blue solid line represents the results from the triangular potential wave for species B, the dark blue solid line represents the total current of species A and B obtained from the triangular potential wave, the light green solid line represents results from the semi-circular potential wave for species A, the medium dark green solid line represents the results from the semi-circular potential wave for species B, and the dark green solid line represents the total current of species A and B obtained from the semi-circular potential wave. The light and dark dotted lines show the peak currents predicted by the Randles-Ševčík equation for species A and B, respectively.

Similar to Figure 4, Figure 6 shows the peak height of the semi-circular current plotted against their corresponding θ_{shift} values at which they are observed with the same color scheme as Figure 4. Although the two maximum points are not as pronounced as in Figure 6 due to the closeness in the formal potential of the two species, we can still see that two lowest points are observed near a θ_{shift} of 0 and -4 , which again correspond with the formal potential of species A and B respectively and is thus still within the limit of detection. Figure 5 and 6 show that a semi-circular potential wave can be used for selective detection of species under conditions where triangular potential waves cannot.

Figure 6: Peak height plotted against the corresponding θ_{shift} value at which it is observed for species A , B , and their total currents obtained through the semi-circular potential wave. The formal potential difference between the two species is -4 dimensionless units, $d_A = 1.0$, and $d_B = 0.5$. The light orange dots represent the peak heights for species A , dark orange dots represent the peak heights for species B , and dark red dots represent the peak heights of the total current.

3.2.3 Two species with formal potential difference of -2 dimensionless units

We next study a case where the formal potential difference between the two species is decreased even further to -2 dimensionless potential units ($\theta_{f,B/D} = \theta_{f,A/C} - 2$), which in dimensional term corresponds to -0.05 V. The color scheme is the same as in Figure 3 and 5 but the results are reported at different θ_{shift} values. Figure 7A corresponds to $\theta_{shift} = -4$, 7B corresponds to $\theta_{shift} = -2$, 7C corresponds to $\theta_{shift} = -1$, 7D corresponds to $\theta_{shift} = 0$, 7E corresponds to $\theta_{shift} = 2$, and 7F corresponds to $\theta_{shift} = 4$.

Here we see that the two individual peaks of species A and B from the triangular potential wave are completely merged in the total current making it impossible to detect the individual species or determine whether there are more than one species. Similarly, the results from semi-circular potential wave cannot be used to detect the individual species as the θ_{shift} value at which the infinite current is observed cannot be associated with the formal potential of either of the species. The total current in Figures 7B, 7C, and 7D all appear to approach infinity, and this trend can be confirmed in Figure 8 as well.

Figure 7: Voltammetric scan obtained using triangular and semi-circular potential waves at different θ_{shift} values for species A and B with a formal potential difference of -2 dimensionless units, which, in dimensional term corresponds to roughly $-0.05V$. The formal potential of species A = 0, $d_A = 1.0$, and $d_B = 0.5$. A is when $\theta_{shift} = -4$, B is when $\theta_{shift} = -2$, C is when $\theta_{shift} = -1$, D is when $\theta_{shift} = 0$, E is when $\theta_{shift} = 2$, and F is when $\theta_{shift} = 4$. The light blue solid line represents the results from the triangular potential wave for species A, the medium dark blue solid line represents the results from the triangular potential wave for species B, the dark blue solid line represents the total current of species A and B obtained from the triangular potential wave, the light green solid line represents results from the semi-circular potential wave for species A, the medium dark green solid line represents the results from the semi-circular potential wave for species B, and the dark green solid line represents the total current of species A and B obtained from the semi-circular potential wave. The light and dark dotted lines show the peak currents predicted by the Randles-Ševčík equation for species A and B, respectively.

Figure 8 shows the peak heights plotted against the θ_{shift} value when the formal potential difference between species A and B is -2 dimensionless units using the same color scheme as Figure 4 and 6. Note the maximum point is observed at a θ_{shift} value close to -1 , which does not correspond to the formal potential of either of the species. However, Figure 7 can be used to infer the presence of more than one species with small formal potential differences due to the wide range of θ_{shift} values where a very large peak is observed, and together with Figure 8 the range of θ_{shift} values in which the formal potential of species A and B might be observed can be estimated. Looking at Figure 7, we see that the total peak current of the semi-circular potential wave results approach infinity approximately between $\theta_{shift} = -2$ and $\theta_{shift} = 0$, and dramatically decreases in the positive θ_{shift} region. This feature can be seen in Figure 8 as well since the peak heights of the total current do not show much variance between the aforementioned range, and decreases rapidly in the far negative and positive region.

Figure 8: Peak height plotted against the corresponding θ_{shift} value at which it is observed for species A , B , and their total currents obtained through the semi-circular potential wave. The formal potential difference between the two species is -2 dimensionless units. The light orange dots represent the peak heights for species A , dark orange dots represent the peak heights for species B , and dark red dots represent the peak heights of the total current.

From the results shown in Sections 3.2.1, 3.2.2, and 3.2.3, the conventional triangular potential sweep is sensitive enough to detect individual species in a mixture when the formal potential difference is significant and in some occasions can be used to determine the diffusion coefficient of a specific species through the Randles-Ševčík equation. However, the results from the semi-circular potential wave is much easier to analyze because of the infinite peak current observed at the formal potential of individual species and its immediate vicinity. The semi-circular potential wave can further be used to distinguish individual species and detect their presence in situations where the triangular potential wave cannot through the suppression and amplification of current contribution at varying θ_{shift} values.

For our analysis we have shifted the potential window with respect to the formal potential of the A/C couple where we set $\theta_{f,A/C}^0 = 0$ and thus $\theta_{shift} = \theta_{avg}$. However, in practice, when the identities of the

species are unknown the only available parameter would be the θ_{avg} value. Therefore in experimental practice, the above analysis would be performed by repeatedly applying the semi-circular potential wave given in Equation (22), where θ_{shift} will be replaced by the θ_{avg} values, until an infinite peak is observed. We showed earlier that the said infinite peak occurs when $\theta_{shift} = 0$ and in its immediate vicinity, thus the formal potential of the species in a mixture can be estimated through the analysis of the voltammograms by determining the θ_{avg} value at which the aforementioned feature is observed.

4 Conclusions

We have introduced a novel approach in running voltammetric scans for electroanalysis on a mixture with two species, A and B , using a semi-circular potential wave with various E_{shift} values where the wave is shifted with respect to the formal potential of one of the species. When the formal potential difference between the two species in a mixture is significantly large, the conventional triangular and the new semi-circular potential waves can both selectively detect the species. However, in situations where the triangular potential wave cannot distinguish individual species due to the small formal potential difference, the semi-circular potential wave can sensitively detect them by showing an infinite increase in the peak current near the formal potentials of the species in the mixture. Under conditions where the formal potential difference between the two species is too small to sensitively detect the individual species using either of the methods discussed, the semi-circular potential wave can still predict the presence of more than one species and estimate the potential range at which their formal potentials may be observed. We thus show that our new method complements the conventional triangular potential wave for electroanalysis.

In this paper we focus on the analytical application of the semi-circular voltammetry method. We note that the infinite scan rate at the apex of the potential wave maximizes the Faradaic current as well as the capacitive current³⁰ and thus that the method operates in a manner such that both signal contributions are amplified. A prior careful determination of the capacitive background though enables the identification of the Faradaic current contribution. We suggest our method primarily as a tool for detecting the presence of a species via its electrochemical signal.

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