

Quenching Behavior of the Electrochemiluminescence of Ru(bpy)₃²⁺/TPrA System by Phenols on a Smartphone-Based Sensor

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Phenolic compounds such as vanillic and *p*-coumaric acids are pollutants of major concern in the agro-industrial processing, thereby their effective detection in the industrial environment is essential to reduce exposure. Herein, we present the quenching effect of these compounds on the electrochemiluminescence (ECL) of the Ru(bpy)₃²⁺/TPrA (TPrA = tri-*n*-propylamine) system at a disposable screen-printed carbon electrode. Transient ECL profiles are obtained from multiple video frames following 1.2 V application by a smartphone-based ECL sensor.

A wide range of detection was achieved using the sensor with limit of detection of 0.26 μM and 0.68 μM for vanillic and *p*-coumaric acids, respectively. The estimated quenching constants determined that the quenching efficiency of vanillic acid is at least two-fold that of *p*-coumaric acid under the current detection conditions. The present ECL quenching approach provided an effective method to detect phenolic compounds using a low-cost, portable smartphone-based ECL sensor.

1. Introduction

Phenolic compounds are phytochemicals widely found in most plant tissues.^[1] In recent years, the presence of these compounds in the agro-industrial processing has led to increased interest in their monitoring, detection and management. For instance, in the agro-bioenergy sector efforts are being made to replace fossil fuels with biofuels to reduce air and land pollution and to stop climate change. However, biofuel production also generates undesired effects. One of them is pollution due to waste materials. Phenolic compounds found in the wastewater (stillage) or feedstock are toxic to microorganisms and thus pollute the soil and fermentation process.^[2]

The detection and quantification of phenols can help engineers to control operating conditions to minimize phenols production, improving biofuel production from non-food lignocellulosic feedstock. Moreover, it is expected that the methods of detection will help companies to better manage the disposal of stillage according to recommended limits.^[3] Such change can minimize soil and groundwater pollution and emission of greenhouse gases.^[3,4]

Chromatographic and mass spectrometric methods are routinely used to detect phenolic compounds.^[5] Although these methods demonstrate outstanding capability to detect trace amounts of phenolic compounds, they require high initial cost, well-trained operators, and a space for lab tests. It also needs expensive columns and regular expensive maintenance. Furthermore, such methods are not available for *in-situ* inspection by environmental agencies. The electrochemiluminescence (ECL) technique has been also used to detect phenolic compounds. In this technique, the ECL quenching mechanism of the Ru(bpy)₃²⁺/TPrA (TPrA = tri-*n*-propylamine) system has been proposed due to energy transfer from the excited state Ru(bpy)₃^{2+*} to quinones formed by electro-oxidation of phenolic compounds.^[6-8] However, expensive traditional instrumentation for ECL sensors such as the photomultiplier tube (PMT) are used in these studies. The biofuel industry demands a physically robust yet affordable and easy-to-use sensor. In the past few years, the use of smartphones incorporated with advanced signal detectors, user-friendly graphical interface, and data processing algorithms is being a growing low-cost sensing tool for different biological and chemical sensing application. In this regard, techniques such as electrochemical detection,^[9] and ECL detection,^[10] both supported by advanced data processing algorithms have been investigated for developing sensitive and rapid assays for analytes detection.

Phenolic compounds could be used to effectively quench the ECL signals generated from the Ru(bpy)₃²⁺/TPrA system based on an intramolecular electron-transfer reaction as described the charge-transfer reactions and homogeneous reactions (Eqs (1)–(8) in Scheme 1). The possible ECL quenching mechanisms occurring in a smartphone-based sensor may be illustrated as follows. The charge-transfer reactions by means of an oxidizing potential (from –1.2 V vs Ag/Ag⁺ to 1.2 V vs Ag/Ag⁺) were assumed to convert Ru(bpy)₃²⁺ into Ru(bpy)₃³⁺, and the neutral form of TPrA to a strong oxidant, the cation radical

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Charge transfer reactions	
$\text{Ru}(\text{bpy})_3^{2+} + \text{e}^- \xrightarrow{k_1} \text{Ru}(\text{bpy})_3^{3+}$	(1)
$\text{TPrA} + \text{e}^- \xrightarrow{k_2} \text{TPrA}^{\bullet}$	(2)
Homogeneous reactions	
$\text{TPrA}^{\bullet} + \text{H}^+ \xrightarrow{k_3} \text{TPrA}^+$	(3)
$\text{Ru}(\text{bpy})_3^{2+} + \text{TPrA}^{\bullet} \xrightarrow{k_4} \text{Ru}(\text{bpy})_3^{3+} + \text{Im}^+$	(4)
$\text{Ru}(\text{bpy})_3^+ + \text{Ru}(\text{bpy})_3^{3+} \xrightarrow{k_5} \text{Ru}(\text{bpy})_3^{2+*} + \text{Ru}(\text{bpy})_3^{2+}$	(5)
$\text{Ru}(\text{bpy})_3^{2+*} \xrightarrow{k_6} \text{Ru}(\text{bpy})_3^{2+} + h\nu$	(6)
$\text{Phenol} + \text{H}_2\text{O} \xrightarrow{k_7} \text{Q} + \text{nH}^+ + \text{ne}^-$	(7)
$\text{Ru}(\text{bpy})_3^{2+*} + \text{Q} \xrightarrow{k_8} \text{Ru}(\text{bpy})_3^{2+} + \text{P}_1$	(8)

Scheme 1. ECL quenching mechanism by phenolic compounds.

TPrA^{•+}, as shown by the charge transfer reactions, Eqs. (1) and (2).^[10–12] In the homogeneous reactions it was assumed that TPrA^{•+} is irreversibly deprotonated to form a free radical, TPrA[•] (Eq. (3)).^[10,11,13] Then, TPrA[•] undergoes an electron transfer oxidation with Ru(bpy)₃²⁺, thus reducing Ru(bpy)₃²⁺ into Ru(bpy)₃⁺, TPrA[•] is also oxidized into its corresponding iminium cation Im⁺ (Eq. (4)).^[10–13] The electron transfer between the oxidized, Ru(bpy)₃³⁺ and reduced, Ru(bpy)₃⁺ precursors, generates the luminophore electronically excited state Ru(bpy)₃^{2+*}, (Eq. (5)), which emits light and relaxes to the ground state species Ru(bpy)₃²⁺ (Eq. (6)).^[10–15] The possible electrooxidation reaction for phenolic compounds is shown in Eq. (7). In this reaction considered irreversible, the phenolic compound is first oxidized to phenoxy radical intermediates which coexist in three isomeric forms, and then to the oxidation products; hydroquinone and catechol. Further, oxidation to *ortho*-benzoquinone or *para*-benzoquinone of such products can occur.^[16–20] In the presence of these reactive quinones (Q), the excited state, Ru(bpy)₃^{2+*} can decay to the ground state resulting in the drop of the ECL intensity through the energy transfer process^[15–17] as shown in Eq. (8), where P₁ represents the reduction product of the quinones.

This study investigated the ECL quenching of the Ru(bpy)₃²⁺/TPrA system by phenolic compounds such as vanillic acid and *p*-coumaric acid. A series of chronoamperometric measurements were performed so that the estimated calibration curve can quantify unknown target vanillic and *p*-coumaric acids containing samples in a range of interest for the biofuel industry. Further, the Stern-Volmer approach is used to determine the quenching coefficients. The efficient ECL quenching of the Ru(bpy)₃²⁺/TPrA system by phenolic compounds using a low-cost portable ECL sensor may provide a new approach in the industrial environments for the determination of these environmentally critical analytes.

Experimental Section

Chemicals

The chemical used in all experiments in this work were: tris (2,2'-bipyridyl) dichlororuthenium(II) hexahydrate (Ru(bpy)₃Cl₂·6H₂O), tri-*n*-propylamine (TPrA), phosphate buffer solutions (PBS), vanillic acid, *p*-coumaric acid and ethanol (all purchased from Sigma Aldrich, St. Louis, MO, USA); and Milli-Q water purchased from APS Water Services Corp., Van Nuys, CA, USA (resistivity ≥ 18.2 MΩ·cm). All these chemicals were used as received.

Sensor Apparatus and Electrodes

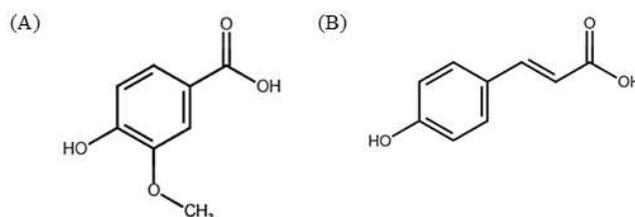
Measurements of sequences of ECL imaging were carried out using a smartphone-based ECL sensor apparatus. In the sensor design a three-electrode set-up compact potentiostat interfaces with a smartphone (Samsung smartphone model) with a custom-made app controlling the phone camera and the potentiostat parameters. Details of the potentiostat circuit operation have been described elsewhere.^[21] Screen-printed carbon electrodes (DropSens, DRP-110) were used for all the experiments. These electrodes consist of a flat ceramic card on which a miniaturized three-electrode system including two carbon electrodes acting as working and counter electrode, and a silver reference electrode are screen-printed. The working carbon electrode is circular with a diameter of 4 mm. The phone camera was set to capture video frames in order to collect two-dimensional (2D) ECL image sequences. The apparatus design and assembly of the portable ECL sensor for its use during operation is presented in previous works.^[21,22]

Assays

The phenolic compounds (Figure 1) were first dissolved in ethanol at 180 mM. The stock solution was then diluted in 0.1 M PBS with 1.0 μM Ru(bpy)₃²⁺ and 20 mM TPrA to provide sample solutions from 0.25 to 30 μM for vanillic acid and 1 to 50 μM for *p*-coumaric acid. These solutions were freshly prepared, and the time passed was recorded as they degraded with time. The samples were discarded after 2 hours. Measurements were performed at room temperature by dropping 50 μL of the sample solution onto the working electrode surface. It was established to wait 10 minutes before taking the measurement, in order to reduce the contact resistance with the electrode. Then, the ECL reaction was triggered by applying 1.2 V, while measuring the ECL emission at the electrode.

Electrochemiluminescence Data Generation

This study used intensity emission data from measurements performed with the smartphone-based ECL sensor to establish calibration curves and explain the quenching mechanism of the system. The ECL was determined given a concentration of phenolic

Figure 1. Molecular structure of (A) vanillic acid, and (B) *p*-coumaric acid.

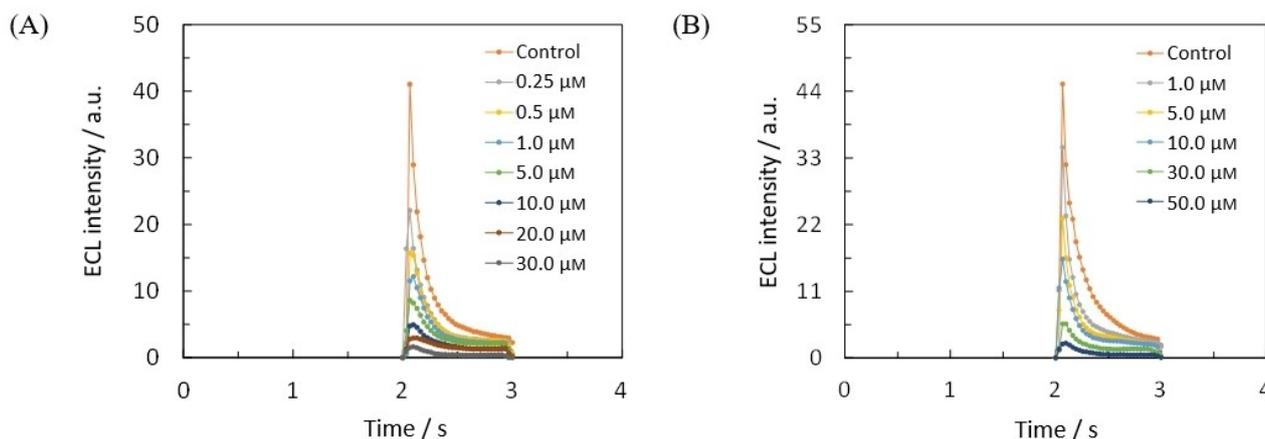


Figure 2. ECL quenching of the system containing $1 \mu\text{M}$ $\text{Ru}(\text{bpy})_3^{2+}$ and 20 mM of TPrA by (A) vanillic acid, and (B) *p*-coumaric acid. A 4 mm diameter of carbon electrode and a potential of 1.2 V vs. Ag/Ag^+ were used for all experiments.

compound. The chronoamperometry technique was used, where a square waveform potential was applied to the working electrode with $50 \mu\text{L}$ of sample solution. The sensor was set to apply a potential of 0 V vs. Ag/Ag^+ for 1 s , followed by -1.2 V vs. Ag/Ag^+ for 1 s in order to stabilize the system while avoiding oxidation of $\text{Ru}(\text{bpy})_3^{2+}$. Then a potential of 1.2 V vs. Ag/Ag^+ for 1 s was applied to produce ECL, which was recorded throughout the stabilization and oxidation periods.

According to the procedure above, several experiments were performed for different concentrations of the phenolic compounds distributed in ranges of $0.25 \mu\text{M}$ to $30 \mu\text{M}$ for vanillic acid and $1 \mu\text{M}$ to $50 \mu\text{M}$ for *p*-coumaric acid. These ranges could be adequate to quantify phenolic compounds present at concentrations between 0.06 and 0.3 g/L in the biofuel production processing reported in previous works.^[2]

2. Results and Discussion

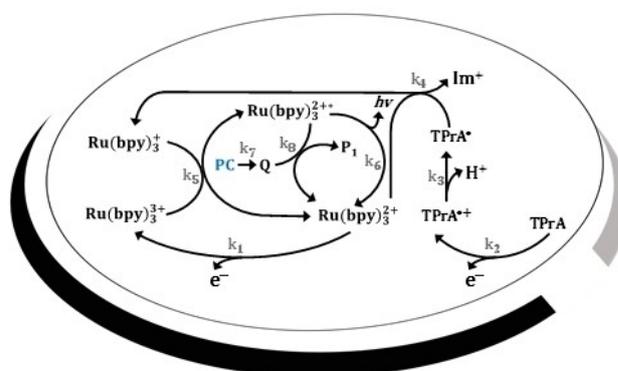
2.1. ECL Quenching by Vanillic and *p*-Coumaric Acids

The ECL quenching assays by phenolic compounds using a portable ECL sensor was performed with $1.0 \mu\text{M}$ $\text{Ru}(\text{bpy})_3^{2+}$ and 20 mM TPrA in 0.1 M PBS. Figure 2 compares the transient ECL intensity for a control solution (with no phenolic compound present) with solutions containing vanillic acid (Figure 2A) and *p*-coumaric acid (Figure 2B). From the control solution results, it can be seen that there exists a sharp increase in the intensity due to the annihilation ECL mechanism which involves the charge transfer between the reduced and oxidized radicals originating from the $\text{Ru}(\text{bpy})_3^{2+}/\text{TPrA}$ system. The ECL intensity occurred after stepping the potential to 1.2 V vs. Ag/Ag^+ . A sharp increase of the intensity is exhibited, reaching a peak, and then progressively decreases over time representing a decay kinetics. It should be noted that a two second delay was set before the potential was stepped in order to stabilize the system and provide for baseline values.

Vanillic acid and *p*-coumaric acid are phenolic compounds with one hydroxyl group substituted aromatic ring system (Figure 1), which could not effectively quench the $\text{Ru}(\text{bpy})_3^{2+}$

photoluminescence.^[17] However, as stated in the homogeneous reaction mechanism of Eq. (7) suggested on the basis of previous studies,^[16–20] the reactive quinones such as *o*- or *p*-benzoquinone produced by the oxidation of phenolic compounds could quench the ECL with a quenching effect on the excited state, $\text{Ru}(\text{bpy})_3^{2+*}$. Scheme 2 shows a schematic representation of the mechanism of the ECL quenching of the $\text{Ru}(\text{bpy})_3^{2+}/\text{TPrA}$ system by phenolic compounds. A previous study coupling a mechanistic model with an optimization algorithm shows promise for the estimation of the parameters k_1 to k_8 governing the reactions shown in Eqs. (1) to (8).^[10] Zheng and Zu^[17] proposed another scheme of the mechanism of the ECL quenching of the $\text{Ru}(\text{bpy})_3^{2+}/\text{TPrA}$ system by phenolic compounds. The authors suggest that in the presence of quencher species, such as reactive quinones, TPrA^* and $\text{Ru}(\text{bpy})_3^+$ might be consumed by their side reactions with the quencher molecules, resulting in the drop of the ECL signal. Thereby, the ECL quenching might also be dependent on the secondary reactions.

As expected, as shown in Figures 2A and B, the ECL emission of the $\text{Ru}(\text{bpy})_3^{2+}/\text{TPrA}$ system decreases with the



Scheme 2. ECL quenching reactions of the $\text{Ru}(\text{bpy})_3^{2+}/\text{TPrA}$ system by the phenolic compounds occurring in the smartphone-based ECL sensor. PC: phenolic compound, Q: reactive quinones.

successive addition of either vanillic acid or *p*-coumaric acid. For instance, the ECL is reduced by ~46%, 79% and 96% with a vanillic acid concentration of 0.25, 5 and 30 μM , respectively. The addition of 1, 10 and 50 μM of *p*-coumaric acid results in ~23%, 64% and 95% of the ECL quenching, respectively. Also, it is clear that when comparing the decay kinetics of vanillic acid and *p*-coumaric acid, there is a difference, which is discussed below in this section based on quenching constants. The ECL profile is an observable output variable that has been used to explore the kinetics of annihilation ECL of the $\text{Ru}(\text{bpy})_3^{2+}/\text{TPrA}$ system in previous studies.^[10]

2.2. Calibration Equations for Vanillic and *p*-Coumaric Acids

The maximum value of the ECL peak intensity was used to derive the calibration curves as shown in Figures 3A and B. It can be seen that the decrease in ECL intensity of the $\text{Ru}(\text{bpy})_3^{2+}/\text{TPrA}$ system is linearly related to the logarithm of the vanillic acid and *p*-coumaric acid concentration in the range from 0.25 to 30 μM and 1 to 50 μM , respectively. The calibration equations are $\text{ECL} = -0.2174 \times \text{vanillic acid} + 0.3484$ with a correlation coefficient (R^2) of 0.961, and $\text{ECL} = -0.4327 \times p\text{-coumaric acid} + 0.7849$ with a R^2 of 0.995. The relatively small normalized standard deviation of the measurements ranging from 0.1% to 6.29%, and 0.19% to 3.4% for vanillic acid and *p*-coumaric acid, respectively, shows that the smartphone-based sensor has good reproducibility. When the concentrations are 30 μM and 50 μM for vanillic acid and *p*-coumaric acid, respectively, an almost complete ECL quenching was observed. The smartphone-based sensor has a wide range for phenolic compounds detection with the limit of detection (LOD) of 0.256 μM for vanillic acid and 0.675 μM for *p*-coumaric acid under the current sensing conditions. It demonstrates that the cell phone camera is well suited for visualized detection.

2.3. Determination of the Quenching Constants

The ECL intensity profiles and the established calibration curves showed an evident difference in terms of the extinction rate between vanillic acid and *p*-coumaric acid. On the basis of this data, measuring of quenching constants through the Stern-Volmer approach provides insights into the mechanisms of the ECL quenching of the $\text{Ru}(\text{bpy})_3^{2+}/\text{TPrA}$ system by vanillic acid and *p*-coumaric acid.

Figures 4A and B show the Stern-Volmer (S-V) plot used to study the role of ECL quenching by phenolic compounds and to determine the quenching rate constants. Conventionally, S-V plots exhibit linear behavior in accordance with the Eq. (9) to study the ECL quenching that can involve a variety of molecular interactions. However, an upward deviation is observed at high concentration of both vanillic acid and *p*-coumaric acid. In these cases, it is suggested that the quenching mechanism could be due to simultaneous dynamic and static quenching.^[23] The ECL dynamic quenching mechanism can be due to diffusive collisions between the phenolic compound (quencher) and the luminophore during the lifetime of the excited state (in this study $\text{Ru}(\text{bpy})_3^{2+}$), not generating ECL intensity.^[24] The static quenching mechanism can be related to the formation of a ground state complex of quencher-luminophore (phenolic compound- $\text{Ru}(\text{bpy})_3^{2+}$), which does not generate ECL intensity; nevertheless, ECL intensity can be emitted by the uncomplexed luminophores after excitation with normal excited state properties.^[25]

The linear S-V equation given by Eq. (9) can be used to determine whether the observed quenching may be due to a collisional mechanism.

$$\frac{I_0}{I} = (1 + K_{sv}Q) \quad (9)$$

where I_0 and I are ECL intensities in the absence and in the presence of the quencher, respectively, Q is the quencher concentration, and K_{sv} ($=k_q\tau_0$) is the S-V dynamic quenching

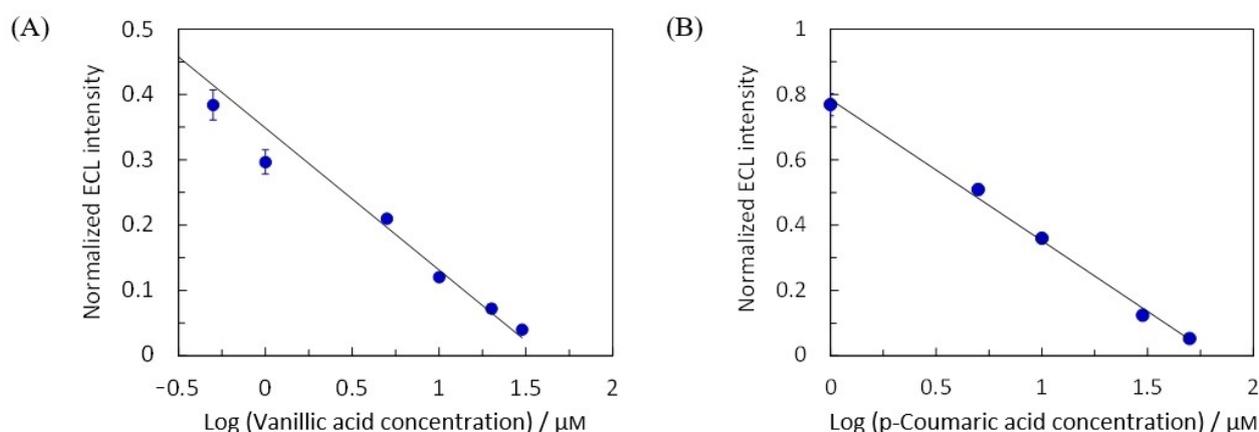


Figure 3. The relationship between the maximum value of the ECL peak intensity and phenolic compound concentration over a range of (A) 0.25 to 30 μM for vanillic acid, and (B) 1 to 50 μM for *p*-coumaric acid with linear regression. ECL experiments were performed with 1.0 μM $\text{Ru}(\text{bpy})_3^{2+}$ and 20 mM TPrA in 0.1 M PBS at a potential of 1.2 V vs. Ag/Ag^+ . The error bars indicate the standard deviation, $n=3$.

rate constant. k_q is the biomolecular quenching constant, and τ_0 is the lifetime of the excited luminophore in the absence of quencher.

The extended S-V equation (Eq. (2)) where there exists a quadratic dependence on the quencher concentration can be used to verify the ground state complex.

$$\frac{I_0}{I} = (1 + K_{sv}Q)(1 + k_qQ) \quad (10)$$

where k_a is the ground state association constant.

Data from Figures 2 and 3 are used to represent the Stern-Volmer plots of ECL quenching by vanillic acid and *p*-coumaric acid as shown in Figures 4A and B, respectively. Table 1 shows the calculated constants for the linear S-V equation (Eq. (9)) and extended S-V equation (Eq. (10)) assuming the lifetime (τ_0) of the excited state, Ru(bpy)₃²⁺ is 600 ns.^[26] S-V constants were calculated using the generalized reduced gradient algorithm embedded in Microsoft Excel.

Figures 4A and B show that the linear S-V equation effectively tracks the desired trajectory of experimental data when considering the range between 0 and 20, and 0 and 30 μ M for vanillic acid and *p*-coumaric acid, respectively. On the other hand, the extended S-V equation was particularly accurate to explain the upward deviation observed at a high vanillic acid and *p*-coumaric acid concentrations as determined by the $R^2 = 0.993$ and 0.998 , respectively.

The quenching constant k_q ($=K_{sv}/\tau_0$) calculated using the Eq. (9) over the linear range of the S-V plots suggests that the

ECL quenching efficiency of vanillic acid is around three times the ECL quenching efficiency of *p*-coumaric acid. Considering the entire range of the S-V plots (entire experimental range of the concentration of quenchers), the values of k_q estimated by Eq. (10) suggests that the quenching efficiency of vanillic acid is around two times the quenching efficiency of *p*-coumaric acid. These results show that either assuming that only the dynamic quenching mechanism occurs (linear relationship of S-V plot) or that the dynamic and static quenching mechanisms occur simultaneously (quadratic relationship of S-V plot), the quenching efficiency of vanillic acid is at least two-fold that of *p*-coumaric acid under the current sensing conditions. The phenolic structure could be a determining factor in the ECL quenching efficiency. Indeed, structurally, vanillic acid belongs to the chemical class of hydroxybenzoic acids, whereas *p*-coumaric acid belongs to the class of hydroxycinnamic acids. Simic et al. found that the measured oxidation potential of these chemical classes were closely related to their structures.^[27] They determined that the introduction of a second hydroxyl group in the benzene ring decreased the oxidation potential. It was also reported that the antioxidant activity of the aromatic compounds increases with the quantity of hydroxyl groups it contains.^[27,28] The results above show that the dependence of the ECL signal in the Ru(bpy)₃²⁺/TPPrA system in the presence of the phenolic compounds follows the Stern-Volmer equations with high accuracy. The quenching constants estimated were able to define quenching efficiencies for either vanillic acid and *p*-coumaric acid. The application of this analysis determining a particular quenching efficiency can be used to characterize

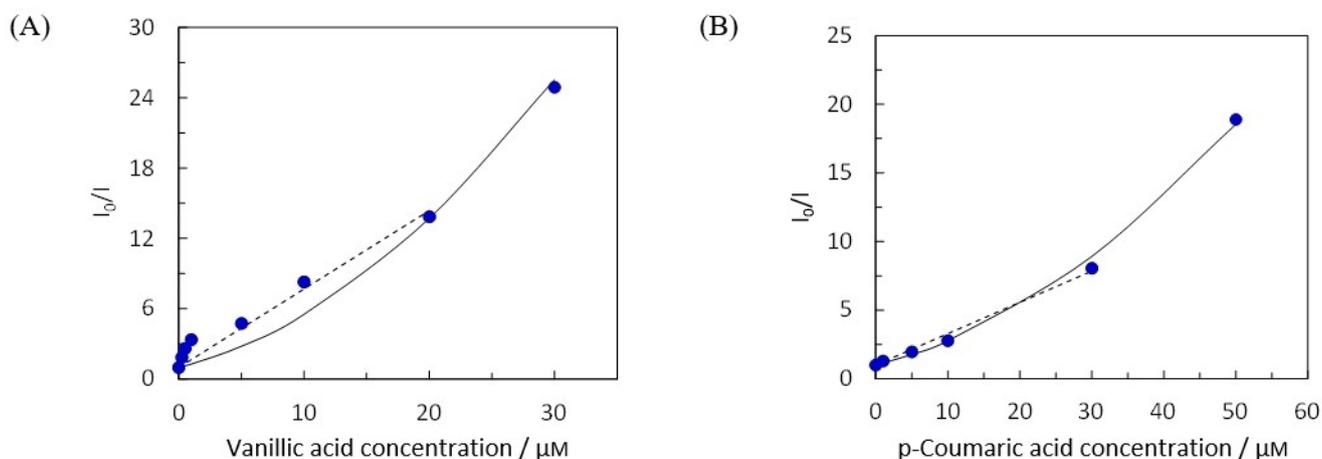


Figure 4. Stern-Volmer plot of ECL quenching of the Ru(bpy)₃²⁺ system by (A) vanillic acid, and (B) *p*-coumaric acid. The dashed and solid curves represent the plots of Eq. (9) (linear S-V equation) and Eq. (10) (extended S-V equation), respectively.

Quencher	Linear S-V equation (Eq. 9)			Extended S-V equation (Eq. 10)		
	R^2	K_{sv} (M ⁻¹)	k_q (M ⁻¹ s ⁻¹)	R^2	K_{sv} (M ⁻¹)	k_q (M ⁻¹ s ⁻¹)
Vanillic acid	0.989	6.69×10^5	1.12×10^{12}	0.993	1.35×10^5	2.25×10^{11}
<i>p</i> -coumaric acid	0.996	2.29×10^5	3.81×10^{11}	0.998	6.61×10^4	1.10×10^{11}

other phenolic compounds found in the biofuel production process, such as syringic acid, syringaldehyde, cinnamaldehyde, among others.

The values of the quenching rate constant K_{SV} for the ECL quenching by vanillic acid and *p*-coumaric acid are close to those obtained previously for the ECL quenching by other phenolic compounds such as hydroquinone ($1.1 \times 10^6 \text{ M}^{-1}$) and catechol ($0.74 \times 10^6 \text{ M}^{-1}$) in the system containing $1.0 \mu\text{M}$ $\text{Ru}(\text{bpy})_3^{2+}$ and 2 mM TPrA in 0.15 M PBS.^[17] Also, in a previous study, we estimated $K_{SV} = 3.99 \times 10^4 \text{ M}^{-1}$ for the ECL quenching by the phenolic compound, dopamine in the system containing $1.0 \mu\text{M}$ $\text{Ru}(\text{bpy})_3^{2+}$ and 20 mM TPrA in 0.1 M PBS.^[22] The estimated K_{SV} values for vanillic acid and *p*-coumaric acid are considered high,^[26] indicating that the sensor is sensitive to quenching from these compounds.

3. Conclusions

This work demonstrated that phenolic compounds such as vanillic acid and *p*-coumaric acid can effectively quench the ECL of the $\text{Ru}(\text{bpy})_3^{2+}$ /TPrA system based on chronoamperometric experiments performed using a smartphone-based ECL sensor. We assumed a mechanism with presence of the reactive quinones generated from phenolic compounds at the carbon electrode surface for the explanation of the ECL quenching behaviour. The dependence of the ECL signal from the portable sensor in the presence of the phenolic compounds followed the Stern-Volmer (S-V) equations with high accuracy. The S-V quenching constants estimated were able to define that the quenching efficiency of vanillic acid is at least two-fold that of *p*-coumaric acid under the current sensing conditions. The wide range of phenolic compounds generated in the biofuel production process could be characterized by determining their quenching efficiencies. The ECL sensor has a wide range of detection with low limit of detection of $0.256 \mu\text{M}$ for vanillic acid and $0.675 \mu\text{M}$ for *p*-coumaric acid. The smartphone-based sensor platform is portable, cost-effective, user-friendly, and also is a field-deployable product. This platform could emerge as a suitable tool for the quantification and detection of phenolic compounds that can be operated in industrial environments improving the biofuel production process.

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: ECL · low-cost sensor · *p*-coumaric acid · vanillic acid · quenching

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