Int. J. Electrochem. Sci., 17 **(2022)** Article Number: 220142, doi: 10.20964/2022.01.26

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Kinetic Determination of 2,7-Dihydroxynaphthalene by Using Belousov-Zhabotinsky Electrochemical Oscillation System

Waqar Uddin

Office of Research Innovation and Commercialization, Bahria University, Karachi Campus, Pakistan
E-mail: vickyfuelche@yahoo.com

Received: 27 September 2021 / *Accepted:* 9 November 2021 / *Published:* 6 December 2021

A new analytical approach for the kinetic determination of 2,7-dihydroxynapthalene (2,7-DHN) by perturbation effect with its narrow concentration range on Belousov-Zhabotinsky (BZ) oscillator catalyzed by tetra-aza-macrocyclic copper complex catalyst ([CuL]$(ClO_4)_2$ was reported in this paper. The Ligand "L" in this complex is 5,7,7,12,14,14-hexemethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene. Perturbation experiments were performed after optimizing the oscillation parameters which indicates that the change in the oscillation amplitude (ΔA) is directly proportional to the concentration of 2,7-DHN added in the range of 4.50×10^{-4} mol L^{-1} to 1.80×10^{-3} mol L^{-1} with the correlation coefficient of 0.98. The calculated relative standard deviation (RSD) from the 6 measurements obtained by the injection of 5.00×10^{-3} mol L^{-1} is 1.90 %. The lower limit of detection (LOD) is 2.10×10^{-4} mol L^{-1}. Factors that influence the oscillation system were studied. A reaction perturbation mechanism was proposed based on a novel FKN model.

Keywords: Oscillating System; Perturbation; Dihydroxynapthalene; Macrocyclic Catalyst; Belousov-Zhabotinsky

1. INTRODUCTION

Chemical oscillation is a type of non-linear chemical dynamics showing periodic changes in the concentration of reactants or products in medium [1][2]. The organized study and the wider field of chemical oscillations is nowadays a concern due to its potential applications in numerous fields comprising chemistry, physics, mathematics, biology and life science. Various electrochemical oscillators [3–9] have been reported but Belousov-Zhabotinsky (BZ) electrochemical oscillator among those have been widely studied and gained worldwide attraction [10][11]. In 1951, the real era of the chemical oscillation began from the invention of Boris Pavlovich Belousov [12], a Soviet biophysicist, his research work on the Krebs-cycle was accidentally turned into the discovery of a famous reaction (oxidation of citric acid by acidic bromate in the presence of cerium ions as a catalyst). According to him, the interconversion of solution color (yellow to colorless to yellow) was due to the single-electron transfer between cerium ions i.e. Ce^{4+} (yellow) and Ce^{3+} (colorless). However, his work was unpublished due to number of objections raised by the publishers. In 1961, Anatol Zhabotinsky, just replaced malonic acid instead of citric acid and cerium sulfate (Ce^{3+}) with manganese sulfate (Mn^{2+}) from Belousov's reaction and got better outcomes as compared to Belousov results. He gave the name to his discovery Belousov-Zhabotinsky (BZ) reaction [13]. After few years, these reactions are focused on their complex mechanism. In this regard, Field, Koros, and Noyes have proposed a well-known FKN mechanism which covers all feasible oscillatory steps [14].

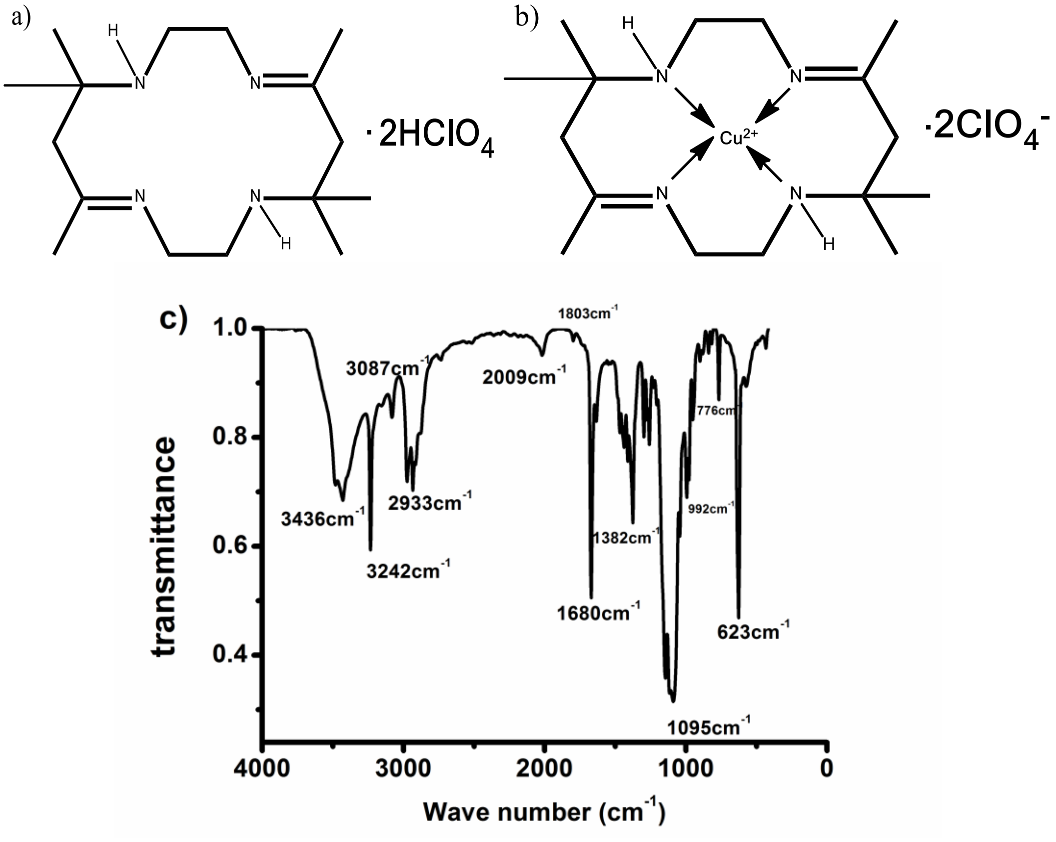


Figure 1. (a). Structure of perchlorate ligand ($L•2HClO_4)_2$; (b). Structure of macrocyclic Cu-Complex catalyst, $[CuL](ClO_4)_2$; (c). IR spectrogram of $[CuL](ClO_4)_2$.

In BZ system, free metal ions catalyst like Ce^{4+} / Ce^{3+} [15] and Mn^{2+} / Mn^{3+} [16] and poly metal ion catalyst like $Fe(phen)_2^{2+}$ / $Fe(phen)_3^{3+}$ [17], $Ru(bpy)_2^{2+}$ / $Ru(bpy)_3^{3+}$ [18] were widely investigated, which is usually refer as classical BZ system. In 1982 Yatimirskii [19], reported a macrocyclic complex of Cu (II) and Ni(II). The use of Cu-complex catalyst $[CuL](ClO_4)_2$ (Figure 1) in the BZ system provides remarkable behaviors usually renowned as conventional system. The color changes in Cu-complex catalyzed BZ system is due to the interconversion of $[CuL]^{2+}$ and $[CuL]^{3+}$ similar to metal ions catalyzed BZ system[10]. Besides citric acid and malonic acid as substrate, various other substrates containing active methylene such as lactic acid [20], malic acid [21] and pyruvic acid [22], acetylacetone [23], etc.

were used in BZ system. Due to high sensitivity, both classic and conventional BZ oscillating systems were utilized for the quantitative determination of various ions, metals, organic and inorganic species [24–27].

In the proposed study, Cu-Complex ($[CuL](ClO_4)_2$) catalyzed BZ oscillator was used as a tool for kinetic determination of 2,7-DHN on their perturbation effect. The Ligand "L" in this complex is 5,7,7,12,14,14-hexemethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene. Oscillation profile was perturbed by the addition of various amounts of 2,7-DHN at the lowest bottom of the 6th cycle resulting decrease in the oscillation amplitude (A). Whereas, the change in the oscillation amplitude (ΔA) of the system was found proportional to the concentration of 2,7-DHN added. Thus, based on the perturbation and ΔA as a parameter, the quantitative approach of kinetic determination of 2,7-DHN is proposed with simpler instrumentation, cost-effective, lower-limit of detection (LOD) and could suppose be extended for the determination of other analytes as well.

2. EXPERIMENTAL

2.1. Apparatus

Experimental assembly of BZ consists of a 50 ml glass reactor in which two electrodes (Platinum (model 213 Shanghai, China) and saturated calomel electrodes (SCE)(Model 217 Shanghai, China)) were dipped. Platinum electrode act as working while SCE serves as a reference electrode and both are connected to a personal computer (PC) through an amplifier (Vernier Software Technology, USA) and Go!link (Vernier Software Technology, USA). Logger lite software (Vernier Software Technology, USA) was used to record potential Vs time data within PC. In overall experiment, the oscillatory mixture was continuously stirred (type 793, Jiangsu, China) at 800 rpm at 25 ^{0}C. Micro-pipette (20–200ul, thermoelectric company of Germany) was used to perturb the oscillation profile.

Cyclic voltammetry experiments were conducted by cyclic voltameter (model CH1660, Shanghai, Chenhua instruments, Ltd, China) consisting 3-electrodes such as 213 Pt-electrode (working electrode), SCE (reference electrode) and Pt-wire (counter electrode). IR test was carried out by an IR-spectrometer (model Nexus-870 Nicolet 380, Shanghai HOMOO Urban Planning Co., Ltd).

2.2. Reagents

All the analytical grade reagents i.e. 98 % H_2SO_4 (Aldrich, China), Na_2BrO_3 (Sinopharm chemical reagent, China), malic acid (Aladdin, China), and 2,7-DHN (Aladdin) were commercially purchased and used without further purification except $[CuL](ClO_4)_2$ which was synthesized in the laboratory by the following two steps and then identified by the IR and chemical analysis techniques.

2.2.1. Synthesis of perchlorate ligand (L•2HClO4)2

In a 500 ml round bottom flask, 126 ml of perchloric acid was mixed drop wisely with 98.5 ml of ethylene-di-amine at a stirring rate of 700 rpm. The apparatus assembly was put into an ice bath to minimize the temperature (0 ^{0}C). When the solution was transparent, 224 ml of acetone was poured into a flask, and the mixture was stirred for 4 hours until the formation of white ppt. The white ppt was filtered, washed using acetone + methanol, and recrystallized, after which white crystals of perchlorate ligand were gotten. Figure 1(a) represents the structure of the perchlorate ligand.

2.2.2. Synthesis of tetra-aza-macrocyclic complex catalyst [CuL](ClO4)2

The 500 ml methanol was poured into a 1000 ml flask containing 48.10 g of perchlorate ligand and 24.90 g of $Cu(Ac)_2.4H_2O$. Under the reflex, the mixture was continuously stirred at a rate of 700 rpm for up to 3-4 hours. When the red ppt appeared, filtered the solution and concentrate the filtrate to its 1/3 original volume. Then, the filtrate was kept for one day. A light red crystal was formed and then filtered and recrystallized from hot methanol. Thus pure crystals of $[CuL](ClO_4)_2$ yielded (Figure 1b).

2.2.3. Infra-Red spectroscopy of tetra-aza-macrocyclic Cu-complex catalyst [CuL](ClO4)2

As can be seen from the infra-red spectrum, the strong absorption peak at 1095 cm^{-1} and the strong absorption peak at 623 cm^{-1} was obtained may be due to the effect of ClO^{4-}. The characteristic stretching vibration peak of C-N appears between a range of 1230-1060 cm^{-1}. The 1382 cm^{-1} is the strong absorption of the C-H characteristic plane vibration peak. The strongest peak at 1680 cm^{-1} is the stretching vibration of C=N, the absorption at 2933 cm^{-1} is the C-H strong stretching vibration peak, maybe 3242 cm^{-1} absorption peak is an N-H stretching vibration peak. In short, the conclusion on the present IR spectrum is that the analyzed compound is $[CuL](ClO_4)_2$.

2.2.4. Elemental analysis of tetra-aza-macrocyclic Cu-complex catalyst [CuL](ClO4)2

The elemental analysis for the Cu-complex catalyst was performed in both theoretical as well as on experimental ways and was concluded that the obtained percentage composition of the elements i.e. C, N, and H by both ways was almost the same within Cu-complex catalyst. The detailed calculations were listed below;

Formula of the Cu-complex catalyst = C16H32N4Cl2O8Cu
Theoretical calculation: C, 35.40 %; N, 10.32 %; H, 5.94 %
Found calculation: C, 35.82; N, 10.32 %, H, 5.936 %.

2.3. Procedure

Chemical reagents were mixed into a glass reactor by the following sequence: 1.5 ml of 0.75 mol

L^{-1} $NaBrO_3$ solution, 29 ml of 1 mol L^{-1} H_2SO_4, 4 ml of 2 mol L^{-1} malic acid solution, and 5.5 ml of 1.85 × 10-2 mol L^{-1} $[CuL](ClO_4)_2$. The total volume of the mixture becomes 40 ml and is continuously homogenized by a magnetic stirrer at 800 rpm. By putting the last reagent into the reactor, the potential Vs time data was recorded into PC through an amplifier and Go!link. The perturbation experiments were carried out by putting various concentrations of 2,7-DHN at the bottom of the 6th cycle and measured the difference in the oscillation amplitude.

3. RESULTS AND DISCUSSION

3.1. Unperturbed and perturb oscillation

By mixing reagents on the above-mentioned sequence, a typical oscillation profile (Figure 2a) between potential vs time was achieved. During oscillation, it was found that the color of the solution was continuously interconverted between red to orange due to the single electron transfer between $[CuL]^{2+}$ (red) and $[CuL]^{3+}$ (orange) [1][10].

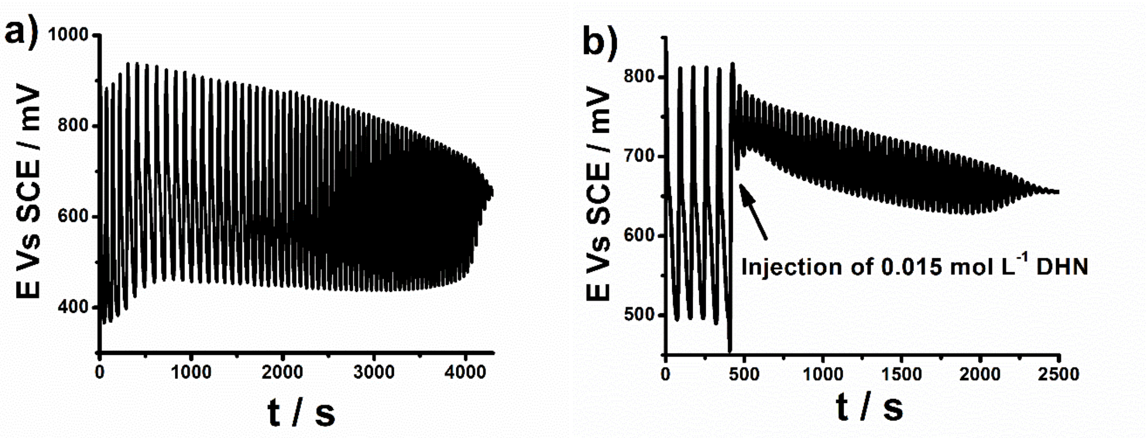


Figure 2. (a). Unpertubed oscillation; (b). Pertubed Oscillation; Common conditions: $[H_2SO_4]$ = 1 M; $[NaBrO_3] = 2.81 \times 10^{-2}$ mol L^{-1}; $[CuL](ClO_4)_2] = 2.54 \times 10^{-3}$ mol L^{-1}; [malic acid] = 2.00×10^{-1} mol L^{-1}; t = 20 ^{0}C; rpm = 800.

The typical oscillation was perturbed by the addition of several amounts of 2,7-DHN at the bottom of the 6th cycle as a result the oscillation amplitude (A) was reduced as mentioned in Figure 2b. The change in the oscillation amplitude (ΔA) was measured and was found proportional to the concentration of 2,7-DHN added. Thus, a new method could be expected to exploit this behavior for the determination of 2,7-DHN.

3.2. Influence of experimental variables

To confirm the maximum probable accuracy and sensitivity in the determination, the influence of the experimental variables (H_2SO_4, Na_2BrO_3, malic acid, $[CuL](ClO_4)_2$, temperature and foreign ions and species on the proposed BZ-oscillator were examined (Figure 2).

Discrepancy in H_2SO_4 amount has remarkably influenced the oscillation profile. The increased concentration of H_2SO_4 could increase the ΔA. A linear regression curve between the concentration of H_2SO_4 Vs ΔA in the range between 0.70 to 1.15 mol L^{-1} was obtained with a correlation coefficient of 0.98 as shown in Figure 3a. Thus, 1 mol L^{-1} H_2SO_4 concentration was selected for experiment because at that concentration the oscillation was uniform.

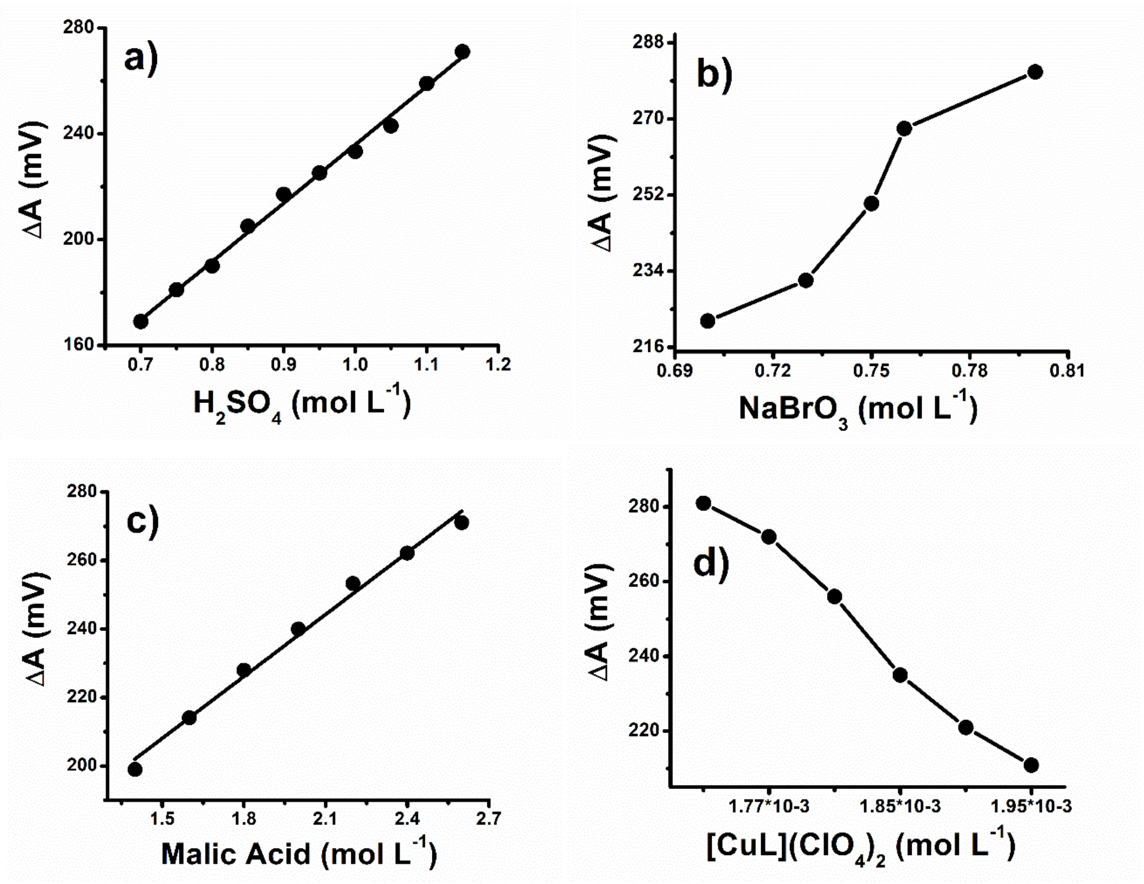


Figure 3. Influence of concentration of reactants on oscillation amplitude: (a). [H_2SO_4] = 0.70 to 1.15 mol L^{-1}; conditions: [$NaBrO_3$] = 2.81 × 10^{-2} mol L^{-1}; [CuL](ClO_4)$_2$] = 2.54 × 10^{-3} mol L^{-1}; [malic acid] = 2.00 × 10^{-1} mol L^{-1}; (b). [$NaBrO_3$] = 0.7 to 0.8 mol L^{-1}; conditions: [H_2SO_4] = 1.00 mol L^{-1}; [CuL](ClO_4)$_2$] = 2.54 × 10^{-3} mol L^{-1}; [malic acid] = 2.00 × 10^{-1} mol L^{-1}; (c). [malic acid] = 1.4 M to 2.6 mol L^{-1}; conditions: [H_2SO_4] = 1.00 mol L^{-1}; [$NaBrO_3$] = 2.81 × 10^{-2} mol L^{-1}; [CuL](ClO_4)$_2$] = 2.54 × 10^{-3} mol L^{-1}; (d). [CuL](ClO_4)$_2$] = 1.75 × 10^{-3} mol L^{-1} to 1.95 × 10^{-3} mol L^{-1}; conditions: [H_2SO_4] = 1.00 mol L^{-1}; [$NaBrO_3$] = 2.81 × 10^{-2} mol L^{-1}; [malic acid] = 2.00 × 10^{-1} mol L^{-1}; t = 20 ^{0}C; rpm = 800.

Variation in the concentration of Na_2BrO_3 was studied over a range of 0.7 to 0.8 mol L^{-1} in BZ system and found that the upsurge amount of Na_2BrO_3 may increase ΔA as indicated in Figure 3b. Thus, for precise determination, the concentration of 0.75 mol L^{-1} is selected as optimum for working due to stable oscillation.

Just like H_2SO_4 and Na_2BrO_3 effects, the influence of malic acid on BZ system was recorded. Briefly, as the concentration of malic acid increase the ΔA of the system increases. Hence, a direct proportional line between the malic acid concentration vs ΔA in the concentration range of 1.40 mol L^{-1} to 2.60 mol L^{-1} was obtained with a correlation coefficient of 0.98 as shown in Figure 3c. Therefore, a middle concentration point (2.00 mol L^{-1}) of malic acid was chosen since it maximizes the stability of oscillation.

We have studied the effects of catalyst from 1.75 × 10^{-3} mol L^{-1} to 1.95 × 10^{-3} mol L^{-1} and the result is shown in Figure 3d which indicated the total opposite influence cause by H_2SO_4, Na_2BrO_3 and malic acid. The upsurge amount of catalyst reduced ΔA of the system. A concentration of 1.85 × 10^{-3} mol L^{-1} was considered optimal because of steady oscillation.

Chemical oscillation is highly sensitive to temperature [28,29]. High-temperature reduces oscillation amplitude (A), oscillation period (T), oscillation number (O_T), oscillation life (O_L) and changes the oscillation mixture muddy result in no oscillation. Therefore, precise and accurate determination the maintaining temperature in oscillation system is highly essential. We trial a series of temperature (4 to 30°C) but select 20 °C for working because at such temperature all the parameters of oscillation (A, T, O_T, O_L) was best fit.

The effect of foreign ions and species were also examined. The BZ oscillating system was influenced by a sample containing 2,7-DHN and various concentrations of interferences. It was found that above 10 % of foreign species producing error of less than 5 % in the determination of 5.00 × 10^{-3} mol L^{-1} 2,7-DHN as indicated in Table 1.

Table 1. Influence of Foreign ions and species on the determination of 5.00 × 10^{-3} mol L^{-1} 2,7-DHN.

Foreign ions and species	Tolerated ratio
Al^{3+}, NH^{4+}, Li^{+}, Na^{+}	2000:1
Ni_2^{+}, Zn^{2+}, Cu^{2+}	1000:1
K^{+}	200:1
CO_3^{-2}	100:1
glucose	10:1
Cl^{-}, Mn^{+2}, $C_2O_4^{2-}$	1:1
Ag^{+}, Fe^{2+}, $Fe3^{+}$, I^{-}	0.1:1

In conclusion, few ions i.e. Ag^{+} & I^{-} have a strong influence on the determination of an analyte, but a huge concentration of Cu^{2+} and most common ions have little effect on the determination.

3.3. Determination of 2,7-DHN

Using the optimal concentration of BZ reagents, perturbation experiments were carried out by the injection of various amounts of freshly prepared 2,7-DHN at the bottom of 6th cycle resulting in the change of oscillation amplitude (ΔA). The interesting feature is that as the concentration of 2,7-DHN within the system increases the ΔA increases. Thus, a linear relationship of 2,7-DHN concentration Vs ΔA in a range of 4.50 × 10^{-4} mol L^{-1} to 1.80 × 10^{-3} mol L^{-1} with the correlation coefficient of 0.98 was achieved as indicated in Figure 4.

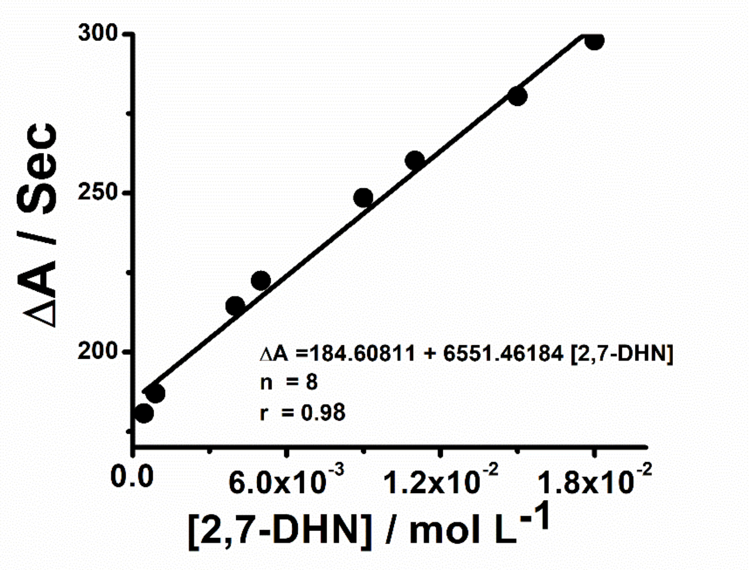


Figure 4. The linear relationship of 2,7-DHN concentration Vs ΔA in a range of 4.50×10^{-4} mol L^{-1} to 1.80×10^{-3} mol L^{-1}; Common conditions: $[H_2SO_4] = 1.00$ mol L^{-1}; $[NaBrO_3] = 2.81 \times 10^{-2}$ mol L^{-1}; $[CuL](ClO_4)_2] = 2.54 \times 10^{-3}$ mol L^{-1}; [malic acid] $= 2.00 \times 10^{-1}$ mol L^{-1}; t = 20 ^{0}C; rpm = 800.

The calibration data was ensured by the following relation (ΔA =184.60811 + 6551.46184 [2,7-DHN]; n = 8; r = 0.98). The calculated relative standard deviation (RSD) from 6 measurements by the injection of 5.00×10^{-3} mol L^{-1} is 1.9 % whereas, the found lower limit of detection (LOD) is 2.10×10^{-4} mol L^{-1}.

3.4. Mechanism

The mechanistic approach of chemical oscillation systems is quite complicated due to kinetic steps consisting of various intermediates species [30]. Therefore, explicating the interaction of analytes with chemical oscillation is extremely challenging. Nevertheless, the renowned FKN mechanism [31] offered by Field et. al is usually accepted which described three processes into 7 oscillatory reactions as under,

Process A

$BrO_3^- + Br^- + 2H^+ \rightleftharpoons HOBr + HBrO_2$ (1)

$HBrO_2 + Br^- + H^+ \rightleftharpoons 2HOBr$ (2)

$HOBr + Br^- + H^+ \rightleftharpoons Br_2 + H_2O$ (3)

$Br_2 + HOOCCHOHCH_2COOH \rightarrow Br^- + H^+ + HOOCCHOHBrCHCOOH$ (4)

Process B

$HBrO_2 + BrO_3^- + H^+ \rightleftharpoons BrO_2^{\bullet} + H_2O$ (5)

$BrO_2^{\bullet} + [CuL]^{2+} + H^+ \rightarrow [CuL]^{3+} + HBrO_2$ (6)

Process C

$HOOCCHOHBrCHCOOH + 6[CuL]^{3+} + 3H_2O \rightarrow$

$6[CuL]^{2+} + Br^- + 2HCOOH + 2CO_2 + 7H^+$ (7)

Process A & B are the main processes because these processes control all the oscillations reactions. The bromide ion (Br^-) is the important reagent in process A. Increase amount of Br^- in the system dominates process A overall oscillatory reactions, as a result, the increase in the potential Vs time was recorded on the working electrode (pt-electrode). The concentration of Br^- was reduced into the system by the occurrence of continuous reactions 1-3, as a result, reaction 1 will be highly affected because reaction 1 is considered to be the rate-determining step in process A. Reaction 4 is the bromination of malic acid. The occurrence of reaction 4 results in a decrease in the amount of Br^- ion. When the amount of Br^- ion is so low to sustain reaction 1, reaction 5 would take place with the production of $BrO_2^\bullet$ radical. The $BrO_2^\bullet$ radical oxidized the $[CuL]^{2+}$ into $[CuL]^{3+}$ via reaction 6. When the concentration of $[CuL]^{3+}$ is large enough into the system, reaction 7 will occur. Thus the automatic switching of process B into process C happens. In reaction 7, the reduction of $[CuL]^{3+}$ into $[CuL]^{2+}$ will take place, and also the amount of Br^- will be increased into the system. When the amount of Br^- ion is large enough to sustain reaction 1, process A becomes dominated again.

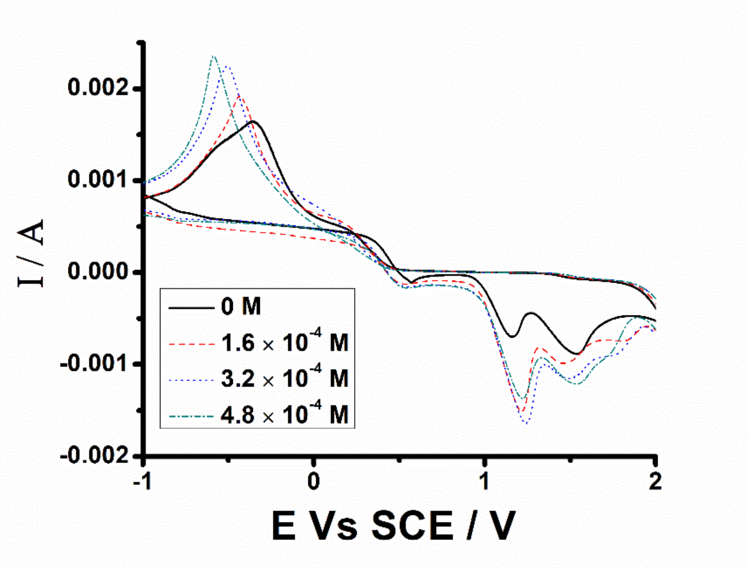
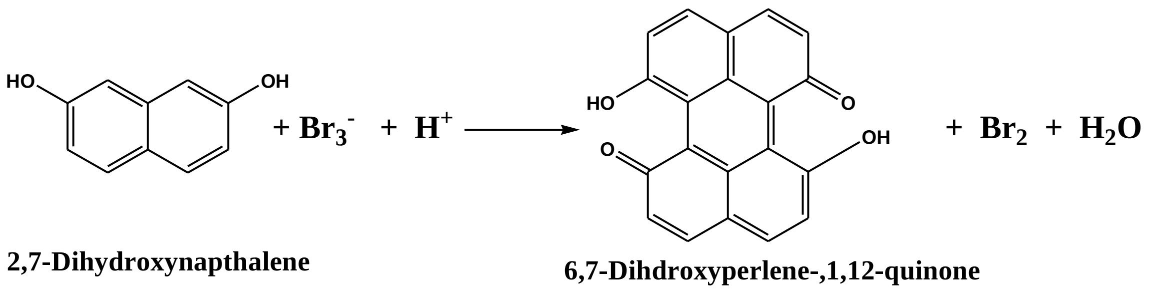
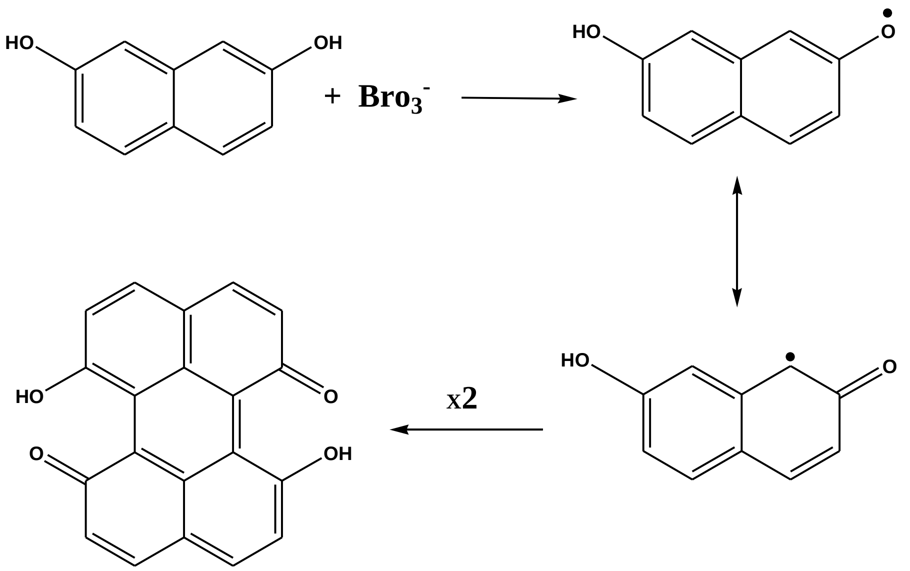


Figure 5. Cyclic voltammogram of the reaction between 2,7-DHN and Iodate, at various amounts of 2,7-DHN; $[NaBrO_3] = 2.81 \times 10^{-2}$ mol L^{-1}; Common Conditions: $[H_2SO_4] = 1$ mol L^{-1}; t = 20 ^{0}C; Scan rate = 100 mV / s.

Cyclic voltammetry (CV) tests were conducted in the presence and absence of 2,7-DHN into the following media; (1)- 1.5 ml of 0.75 mol L^{-1} $NaBrO_3$ + 38.50 ml of 1 mol L^{-1} H_2SO_4; (2)- 4.00 ml of 2.00 mol L^{-1} malic acid + 36 ml of 1.00 mol L^{-1} H_2SO_4; (3)- 5.50 ml of 1.85×10^{-2} mol L^{-1} $[CuL](ClO_4)_2$ + 34.5 ml of 1 mol L^{-1} H_2SO_4 to confirmed whether analytes react to reactant, product or intermediate species. It has been observed from the cyclic voltammograms that only $NaBrO_3$ shows a redox reaction with 2,7-DHN (Figure 4). Thus, based on the result of CV and published literature[32], the following reaction 8 is proposed and added to the FKN mechanism.



(8)



(8a)

Acidic solution of BrO_3^- oxidized 2,7-DHN into quinone along with the generation of Br_2 as byproduct via reaction 8. Increase amount of Br_2 consumed by reaction 4 and at same time push reaction 3 in the reverse direction to enhance HOBr concentration. The upsurge amount of HOBr reverse reaction 2 enriching $HBrO_2$ concentration. The accumulation of both HOBr & $HBrO_2$ has reduced the rate of reaction 5 and pushes reaction 6 in reverse direction to increase CuL^{2+} concentration to some extent via reaction 6. Thus, a decline in the potential was noticed which reflects in decrease oscillation amplitude as indicated in Figure 2b.

4. CONCLUSION

Based on the perturbation effect, we proposed a novel technique for the determination of 2,7-DHN using BZ oscillation. Injection of various amounts of 2,7-DHN into BZ oscillation could reduce the oscillation amplitude which is directly related to the concentration of analyte in the range of 4.50×10^{-4} mol L^{-1} to 1.80×10^{-3} mol L^{-1} with the correlation coefficient of 0.98. The proposed reaction mechanism was justified by FKN mechanism and CV outcomes.

References

1. W. Uddin, G. Hu, X. Sun, H. Zhang, Y. Wang, L. Hu, *Arab. J. Chem.* (2017) 3–11.
2. W. Uddin, G. Hu, L. Hu, X. Shen, Z. Fang, Y. Zhang, J. Song, *Int. J. Electrochem. Sci*, 12

(2017) 178–191.
3. S. Anić, J. Maksimović, D. Lončarević, N. Pejić, Ž.D. Čupić, *Russ. J. Phys. Chem. A*, 83 (2009) 1468–1472.
4. W. Uddin, G. Hu, L. Hu, Y. Hu, Z. Fang, R. Ullah, X. Sun, Y. Zhang, J. Song, *J. Electroanal. Chem.*, 803 (2017) 135–140.
5. W. Uddin, G. Hu, X. Sun, S. Ullah, S. Sardar, Z. Wangning, M.Y. Nawabi, *Int. J. Electrochem. Sci.*, 13 (2018) 598–609.
6. W. Uddin, S. Ullah, S.U. Rehman, G. Hu, M.Y. Nawabi, Z. Fang, S. Sardar, R. Ullah, *CHIANG MAI J. Sci.*, 46 (2019) 1207–1218.
7. W. Uddin, G. Hu, L. Hu, Y. Hu, Z. Fang, S. Ullah, X. Sun, X. Shen, J. Song, *Int. J. Electrochem. Sci*, 12 (2017) 4193–4203.
8. Y. Zhou, W. Uddin, G. Hu, *Microchem. J.*, 160 (2021) 105617.
9. L. Zhang, W. Uddin, G. Hu, X. Shen, L. Hu, *Microchem. J.*, 168 (2021) 106380.
10. M.Y. Nawabi, G. Waqar Uddin, S. Ullah, Z. Fang, S. Sardar, *Int. J. Electrochem. Sci*, 14 (2019) 8676–8685.
11. G. Hu, Q. Wang, M. Meng, M.Y. Lu, F.S. Zhao, L. Hu, *J. Chem.*, 9 (2012) 1412–1421.
12. A. Pechenkin, *J. Biosci.*, 34 (2009) 365–371.
13. A.M. Zhabotinsky, A.B. Rovinsky, *J. Stat. Phys.*, 48 (1987) 959–975.
14. R.J. Field, *J. Am. Chem. Soc.*, 94 (1972) 8649.
15. Z. Noszticzius, J. Bodiss, *J. Am. Chem. Soc.*, 101 (1979) 3177–3182.
16. M.C. Guedes, R.B. Faria, *J. Phys. Chem. A*, 102 (1998) 1973–1975.
17. K. Kurin-Csörgei, A.M. Zhabotinsky, M. Orbán, I.R. Epstein, *J. Phys. Chem.*, 100 (1996) 5393–5397.
18. F. Bolletta, V. Balzani, *J. Am. Chem. Soc.*, 104 (1982) 4250–4251.
19. K.B. Yatsimirskii, L.P. Tikhonova, L.N. Zakrevskaya, Y.D. Lampeka, A.G. Kolchinskii, *React. Kinet. Catal. Lett.*, 21 (1982) 381–386.
20. J. Wang, S. Yang, R. Cai, Z. Lin, Z. Liu, *Talanta*, 65 (2005) 799–805.
21. G. Hu, L. Chen, J. Zhang, P. Chen, W. Wang, J. Song, L. Qiu, J. Song, L. Hu, *Cent. Eur. J. Chem.*, 7 (2009) 291–297.
22. G. Hu, L. Hu, Z. Xu, F. Xie, S. Ni, *Asian J. Chem.*, 16 (2004) 1063.
23. Z. Ke, M. Wanhong, C. Ruxiu, L. Zhixin, G. Nanqin, *Anal. Chim. Acta*, 413 (2000) 115–123.
24. L. Chen, G. Hu, J. Zhang, L. Hu, *Mendeleev Commun.*, 19 (2009) 224–226.
25. L. Hu, G. Hu, H.-H. Xu, *J. Anal. Chem.*, 61 (2006) 1021–1025.
26. P. Chen, G. Hu, W. Wang, J. Song, L. Qiu, H. Wang, L. Chen, J. Zhang, L. Hu, *J. Appl. Electrochem.*, 38 (2008) 1779–1783.
27. L. Hu, J. He, G. Hu, *Asian J. Chem.*, 25 (2013) 2933.
28. E. Koros, M. Orban, Z. Nagy, *J. Phys. Chem.*, 77 (1973) 3122–3123.
29. S. Sen, S.S. Riaz, D.S. Ray, *J. Theor. Biol.*, 250 (2008) 103–112.
30. Y. Luo, M. Orban, K. Kustin, I.R. Epstein, *J. Am. Chem. Soc.*, 111 (1989) 4541–4548.
31. R.J. Field, E. Koros, R.M. Noyes, *J. Am. Chem. Soc.*, 94 (1972) 8649–8664.
32. W. Zhang, W. Uddin, G. Hu, L. Hu, Z. Fang, *J. Electroanal. Chem.*, 823 (2018) 378–387.