Short Communication

Determination of Ascorbic acid by Using a Belousov-Zhabotinsky Oscillating System Catalyzed by a Macrocylic Complex

Saif Ullah[1], Waqar Uddin[1], Gang Hu[1], Muhammad Yasir Nawabi[1], Rooh Ullah[2], Saira Sardar[3], Muhammad Mustaqeem[4], and Xiaofeng Shen[1]*

[1]Department of Chemistry, Anhui University, Hefei, 230601, People's Republic of China
[2]Department of Chemistry, University of Turbat-92600, Balochistan, Pakistan
[3]Institute of Chemical Science, University of Peshawar, Pakistan
[4]Department of Chemistry, University of Sargodha Sub Campus Bhakkar, Pakistan
[*]E-mail: hugang@ustc.edu

An appropriate analytical technique for determination of ascorbic acid (AA) by its perturbation effect on Belousov-Zhabotinskii (BZ) oscillating system was reported in this article. The macrocyclic copper (II) complex ($[CuI(ClO_4)_2]$) was used as a catalyst while malic acid as substrate in BZ system. The ligand L in the macrocyclic-complex is 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene. Experimental outcomes shown the perturbation effect of AA could cause the change in the amplitude of oscillation (ΔA) and change in the period of oscillation (ΔT) which were directly related to its concentration (3×10^{-6} to 1.05×10^{-4} M) with correlation coefficient of 0.99 respectively. The calculated relative standard deviation (RSD) is 2.71 % by eight samples (1.2×10^{-5} M) and the observed lower limit of detection is 1.5×10^{-6} M. The cyclic voltammetry (CV) experiments were used to confirm the redox reaction between ascorbic acid and sodium bromate. Furthermore, the reaction perturbation mechanism, was derived from the well-known FKN (Field-Koros-Noyes) oscillation mechanism.

1. INTRODUCTION

The chemical oscillation is a non-linear phenomenon, showing a continuous changing due to the involvement of intermediate species. So far, hundreds of chemical oscillators has been reported such as Belousov-Zhabotinsky (BZ) [1], Bray-Liebhafsky (BL) [2,3], Briggs-Rauscher (BR) [4-7] and hydrogen

peroxide-ferrocyanide oscillator system etc. [7,8]. Among them BZ oscillator is thoroughly studied. In specific BZ system, the oxidation of organic substrate is accomplish by $NaBrO_3^-$ solution (acidic) with the help of metal ions i.e. $Cerium^{+4}$, $Maganese^{+2}$, Ferron ($Fe(phen)_3^{+2}$) and $Ru(biphy)_3^{+2}$ or tetra-aza-macrocyclic Cu-complex catalyst ($[CuL](ClO_4)_2$). For the first time, Tichonova [9,10], utilized pulse perturbation technique (PPT) using oscillating system (BZ) for analyzing samples which has attracted the attention of world wise scientists in the field of quantitative analysis. Among the used catalysts in the BZ system, $[CuL](ClO_4)_2$ could be consider as the best catalyst because of their existence Pi-bond in the ligand L (5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene) which indorse a higher reaction kinetics including electron donating at each steps in oscillatory reaction [11], less activation energy, huge frequency and exposed to exterior perturbation. Such behaviors of $[CuL](ClO_4)_2$ favors it uses as best catalyst in BZ oscillator for determination of compounds.

During $[CuL](ClO_4)_2$-catalyzed BZ oscillator, a continuous electron is exchange between its oxidize $[CuL]^{3+}$ catalyst and reduce $[CuL]^{2+}$ form in a repeated manner. The $[CuL]^{2+}$ appear in red color while the $[CuL]^{3+}$ appeared as orange. Thus, the color of BZ oscillator was exchange between $[CuL]^{2+}$ and $[CuL]^{3+}$ and its data was collected in PC. Up till now, our group has successfully utilized macrocyclic Cu-complex catalyzed BZ oscillator for determination of alizarin red S [12], calcium pantothenate [13], paracetamol [14], Ag^+ [15], pyrogallol [16], vitamin B6 [17], xylenol orange [18], and catechol [19].

In this article, we used BZ oscillating system as a tool for the determination of an ascorbic acid (AA) by its perturbation technique. The effect of AA replicated as a changed in the oscillation amplitude (ΔA), which is linearly proportional to its concentration (3×10^{-6} M to 1.05×10^{-4} M) with correlation coefficient of 0.9917. The cyclic voltammetry (CV) was used to confirm the redox reaction between AA and sodium bromate. The reaction perturbation mechanism was derived from the well-known oscillating FKN mechanism.

2. EXPERIMENTAL

2.1. Reagents

All the reagents i.e. $NaBrO_3$ (Sinopharm Chemical reagent, China), malic acid (Aladdin, Shanghai, China), ascorbic acid (Aladdin, Shanghai, China) and sulfuric acid (Aldrich 98 %) were used of an analytical grade with no additional refining. Only $[CuL](ClO_4)_2$ was prepared by available literature [20] and characterized by Infra-Red (IR) spectroscopy and elemental analysis. Solution of 00.75 M sodium bromate, 2.00 M malic acid, 0.084 M $[CuL](ClO_4)_2$ were prepared within 1.00 M of H_2SO_4. Freshly prepared solutions of ascorbic acid were prepared in such 1.00 M of H_2SO_4 and then used to perturb the oscillations.

2.2. Apparatus

The BZ oscillation setup consist of a 50 ml of glass vessel and potential recording tools. The 50 ml glass vessel was fixed with temperature regulator device (thermostat model-DZCS-IIC) which kept the temperature of solution upto18 ± 0.5°C. With the help of magnetic stirrer model 79-3 (Jiangsu, China)

the mixture was standardize at 750 rate per minute. Pt-electrode (type 213, Shanghai, China) used as a working electrode while saturated calomel electrode (SCE) (Model 217 Shanghai, China) act as a reference electrode. Both electrodes were linked to PC through Go!Link and amplifier. The data (potential vs time) was analyzing by logger-lite software.

The cyclic voltammetry (CV) experiments was carried out by cyclic voltammeter (model CH1660, Shanghai, Chenhua instruments, Ltd, China).
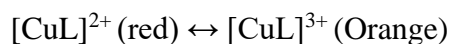
2.3. Procedure

For the BZ oscillation system, the 40 ml oscillatory solution were mixed into reaction vessel by given sequence: 01.00 ml of 0.75 M $NaBrO_3$, 28.5 ml of 1.00 M H_2SO_4, 4 ml of 2.00 M malic acid solution, and 6 ml of 0.084 M $[CuL](ClO_4)_2$. The Pt-electrode and SCE-electrode were inserted into the reaction vessel. Both electrodes were connected to PC and potential versus time were recorded in it. For perturbations experiments, various concentrations of ascorbic acid were used to perturb the oscillation profile.

The cyclic voltamogram were obtained in the absence and presence of additives (ascorbic acid) into the acidic solution of each BZ reagents e.g. (1.00 ml of 0.75 M sodium bromate + 39 ml of 1.00 M sulfuric acid), (4 ml of 2.00 M malic acid + 36 ml of 1.00 M sulfuric acid) and 6 ml of 0.084 M $[CuL](ClO_4)_2$ + 34 ml of 1.00 M sulfuric acid). The total volume for CV experiments were kept 40 ml by adjusting the volume of sulfuric acid.

3. RESULTS AND DISCUSSIONS

3.1. Typical oscillation for BZ oscillator

Typical oscillating pattern (Fig. 1a) for BZ system was achieved by the combination of oscillating solutions. The known phenomena of chemical oscillation display a repeated variation in the amount of few species that are replicate in repetitive colors, pH or redox-potential dissimilarities, depending on the precise system [21]. For $NaBrO_3$-sulfuric acid-malic acid-$[CuL](ClO_4)$, the repeated deviation were noticed in a form of continuous color change (red-orange-red) throughout oscillation as shown below,.

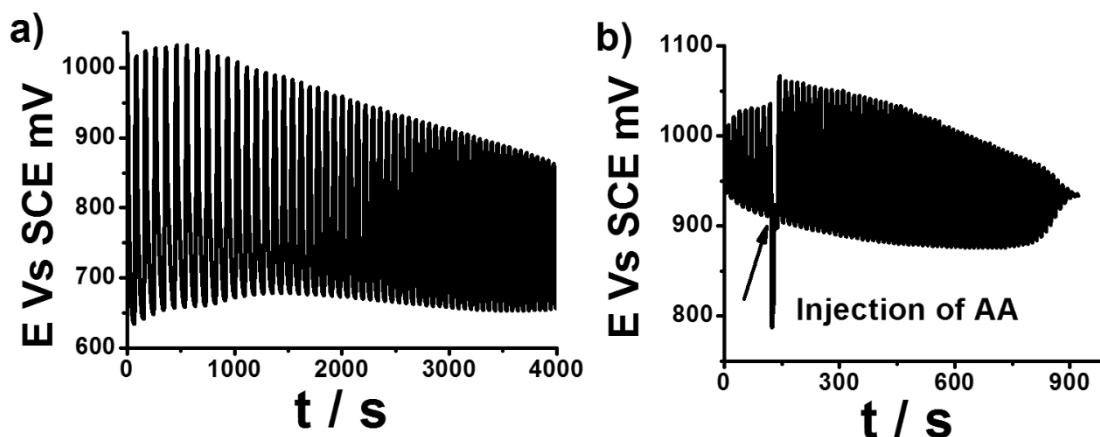$$[CuL]^{2+} \text{ (red)} \leftrightarrow [CuL]^{3+} \text{ (Orange)}$$

Figure 1. Oscillation profiles for the proposed B-Z oscillator in the absence and presence of ascorbic acid by the perturbation using Pt vs SCE electrodes, a): [AA] = 0.000 M; b): [AA] = 1.2×10^{-5} M; Common condition: [NaBrO$_3$] = 0.01875 M; [malic acid] = 0.2 M; [H$_2$SO$_4$] = 1.0 M; [CuL](ClO$_4$)$_2$ = 1.36×10^{-3} M, t = 17 ^{O}C.

3.2. Influence of experimental variables

Oscillating chemical system are easily effected by experimental variables. In order to find the optimal environment for determination of AA, the influence in the amount of oscillating solutions i.e. NaBrO$_3$, H$_2$SO$_4$, malic acid and catalyst were observed. The optimum values for working conditions are usually recognized by 3-situations i.e. (1) achieving extreme change in the oscillation amplitude (ΔA), certifying the high sensitivity for the determination of AA; (2) a huge accurately are shown due to the perturbation of AA (3) confirming the maximum stability of chemical oscillation with respect to time, such properties is highly important to achieve good results. The influence of precise experimental variables on BZ system were observed due to the presence and absence of AA. The ΔA (=A2-A1) and ΔT (=T2-T1) were consider as working parameters. Whereas, (A2, T2) and (A1, T1) are the amplitude and period of oscillation after and before injection respectively [22].

The effect in the variation of malic acid concentration was tested from 0.12 M to 0.42 M. As the amount of malic acid increased into the system, the ΔA was decrease while ΔT increase as shown in Fig 2a. Thus, a concentration of 0.19 M of malic acid was selected as optimal for working.

The [CuL](ClO$_4$)$_2$ concentration was varied from 0.0012 M to 0.0048 M. Both, ΔA and ΔT were incredible effected with increase concentration of [CuL](ClO$_4$)$_2$ as shown in Fig. 2b. At increase concentration of [CuL](ClO$_4$)$_2$, ΔA and ΔT were first decrease and then increase with increasing concentration of [CuL](ClO$_4$)$_2$. The concentration of 0.0034 M [CuL](ClO$_4$)$_2$ was chosen as optimal because at this concentration the oscillation was uniform.

The influence of NaBrO$_3$ concentration was examine from 0.0044 M to 0.092 M. It was found that the increasing concentration of NaBrO$_3$ into system led to increase ΔA and ΔT as mention in Fig 2c. Thus, 0.054 M concentration for NaBrO$_3$ was selected for AA determination.

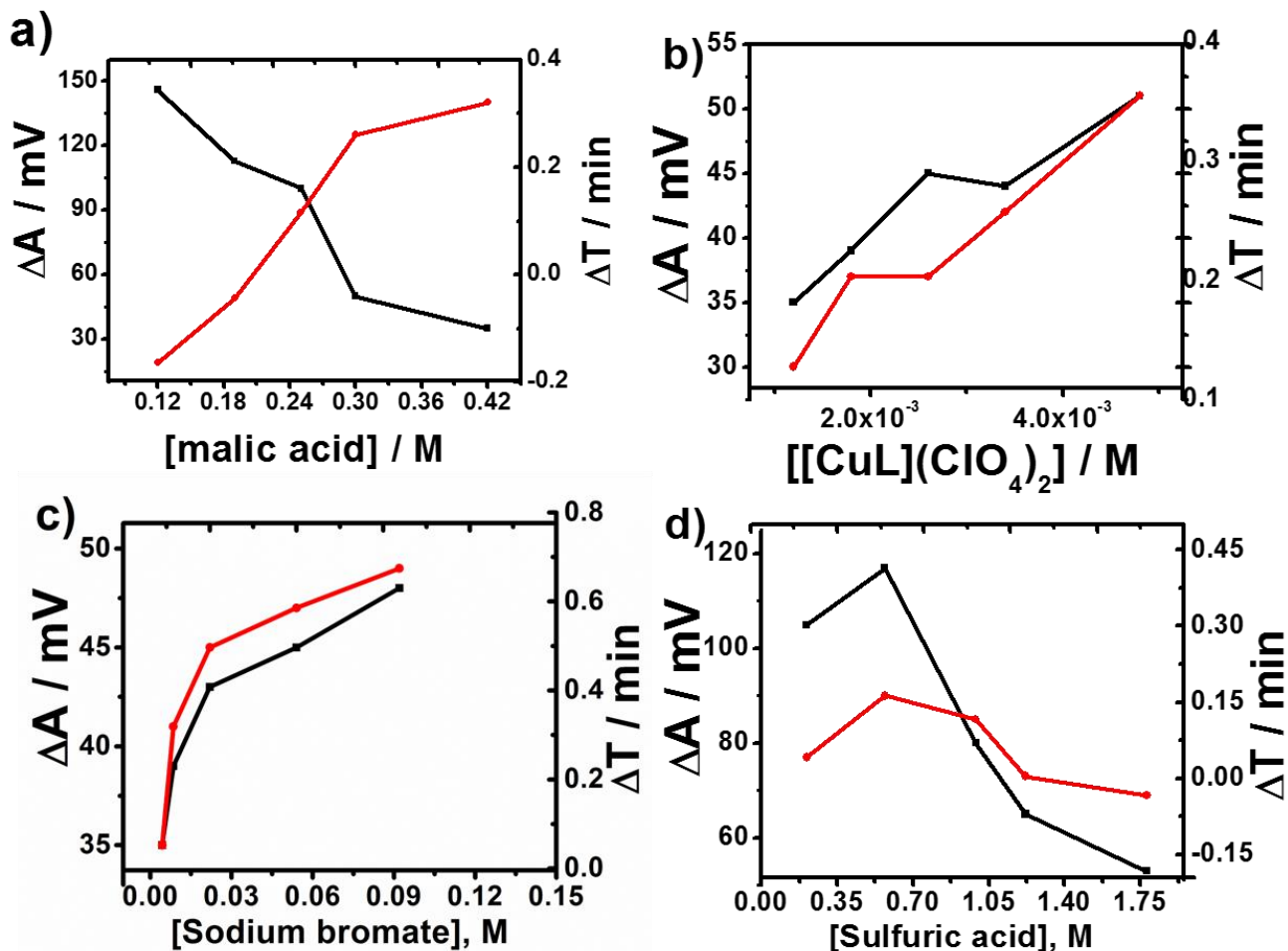**Figure 2.** Influence of the concentration (a) malic acid, (b) [CuL](ClO$_4$)$_2$, (c) sodium bromate, (d) sulfuric acid on the ascorbic acid perturb oscillation system (● refers to Δ amplitude and ▪ refer to period) Condition: (a) [CuL](ClO$_4$)$_2$ = 1.36 × 10^{-3} M, [NaBrO$_3$] = 0.01875 M, [H$_2$SO$_4$] = 1.0 M, [AA] = 1.2 × 10^{-5} M. (b) [malic acid] = 0.2 M, [NaBrO$_3$] = 0.01875 M, [H$_2$SO$_4$] = 1.0 M, [AA] = 1.2 × 10^{-5} M. (c) [malic acid] = 0.2 M, [CuL](ClO$_4$)$_2$ = 1.36 × 10^{-3} M, [H$_2$SO$_4$] = 1.0 M, [AA] = 1.2 × 10^{-5} M. (d) [malic acid] = 0.2 M, [CuL](ClO$_4$)$_2$ = 1.36 × 10^{-3} M, [NaBrO$_3$] = 0.01875 M, [AA] = 1.2 × 10^{-5} M.

The variation in the concentration of sulfuric acid was investigated over the range from 0.21 to 1.78 M and was found that as concentration of sulfuric acid were increased into the system, the ΔA increase while ΔT was decrease as indicated in Fig. 2d. A 1.22 M sulfuric acid concentration was considered as ideal point, because at this concentration the oscillation is more stable.

A [CuL](ClO$_4$)$_2$-BZ system is highly influence by temperature [23], that is why, the effect of temperature was measured in between 15 to 25˚C. We found that, above and below 25˚C, the ΔA and ΔT were not accurate. Thus, 25˚C was chosen as optimal.

The effect of magnetic stirring (300-1200 rmp) was also measured and 500 rmp was consider for operational.

Table 1. Influence of foreign ions and species on the determination of Ascorbic acid

Foreign ions and species	Tolerated ratio
Al^{3+} , Ni^{2+} , Li^+	10000
K^+ , NH^{4+}	2000
Mg^{2+} , Mn^{2+} , Zn^{2+} , Ac^- , Cu^{2+}	1000
Na^+	500.0
Cl^-	10.0
F^-	100.0
Br , Ag^+	0.10
Fe^{3+} , $H_2PO_4^-$	5.00
I^-	0.01
Fe^{2+}	0.005

Chemical oscillation are simply affected due to the existence of foreign substances. Therefore, the effect of few foreign species were investigated over BZ system as shown in Table 1. The BZ oscillator based on $[CuL]^{2+}$ catalyzed system, the effect of sum of foreign species, cause an error of less than 5% in the determination of 1.5×10^{-6} M AA was altered as the tolerance limit as indicated in Table 1. Some foreign species have strong interference, such as I^-, Cl^-, Ag^+ and Br^-. Normally, the characteristic of the ions and species often have a strong effect on the level of analyte tolerate.
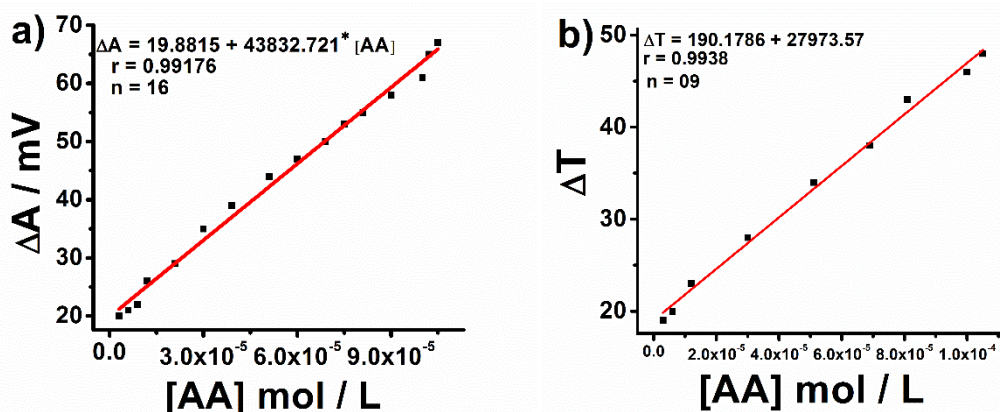
3.2. Determination of ascorbic acid

Figure 3. (a). Calibration curve of the change in the in oscillation amplitude vs ascorbic acid; (b). Calibration curve of the change in the oscillation period vs ascorbic acid; Common Condition: Concentration range of 3×10^{-6} to 1.05×10^{-4} M; $[NaBrO_3] = 0.01875$ M; [malic acid] = 0.2 M; $[H_2SO_4] = 1.0$ M; $[CuL](ClO_4)_2 = 1.36 \times 10^{-3}$ M, t = 17 °C.

For determination of AA, different amounts of AA were used to perturb the BZ system as a result the ΔA and ΔT were found. We further notice that, as the concentration of AA into the system were increased the ΔA and ΔT were increase. Thus the linelly proportional curves was achieved between AA concertation *vs* ΔA and ΔT in a concentration range of 3×10^{-6} M to 1.05×10^{-4} M with correlation

coefficient of 0.99 respectively as shown in Fig. 3a and Fig.3b respectively. The calibration data was obtained by the following equation:

$\Delta A = 19.88155 + 43832.9721$[ascorbic acid], (r = 0.99176), (n = 16)

The calculated relative standard deviation (RSD) was obtained by eight measurements of 1.2×10^{-5} M of AA was 2.7 %. The lower limit of detection (LOD) is 1.5×10^{-6} M obtained. Such accuracy in the determination of AA are quite acceptable.

To check the preciseness of our proposed BZ methodology, the known concentration of AA were put into the standard liquors (shown in Table 2), and repeated the identical process. The recovery results shown the accuracy of our proposed method, lies from 92.24 to 100.80 which is consider best. Furthermore, the obtained determination results of AA by BZ oscillator was compared with few instrumental techniques as indicated in Table 3 and were found that our proposed method is quite accurate and acceptable for the determination of AA or for other compounds as well.

Table 2. Determination results and recovery for AA

Sample	Known Concentration / 10^{-5} M	Added Concentration / 10^{-5} M	Found Concentration / 10^{-5} M	Recovery %
1	0.29	0.2	0.452	92.24
2	0.55	0.2	0.756	100.80
3	0.95	0.2	1.145	99.60
4	1.10	0.2	1.281	95.00
5	2.00	0.2	2.080	94.55
6	2.80	0.2	2.992	99.70
7	3.70	0.2	3.882	99.50
8	5.00	0.2	5.046	96.00

* Common condition: [NaBrO$_3$] = 0.01875 M; [malic acid] = 0.2 M; [H$_2$SO$_4$] = 1.0 M; [CuL](ClO$_4$)$_2$ = 1.36×10^{-3} M, t = 17 ^{O}C.
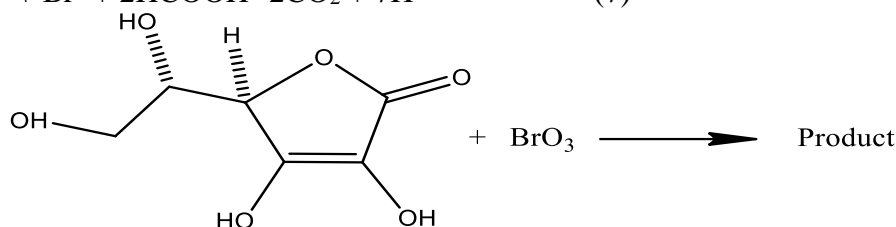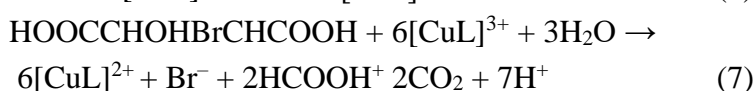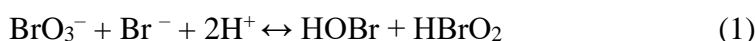
Table 3. Comparison of AA determination by BZ oscillator with few instrumental techniques

Techniques	Linear Range	Correlation Coefficient	(RSD) %	Reference
BR Oscillator	3×10^{-6} to 1.05×10^{-4} M	0.9917	2.7	
Cyclic voltammetry	1.97×10^{-4} to 9.88×10^{-4} M	0.9950	>1.5	[24]
Cyclic voltammetry	1.00 to 1.75 ug/ml	0.9977	0.83	[25]
HPLC	0.25 to 1.5 mg mL^{-1}	0.9998	1.87	[26]
Spectrophotometric	5×10^{-7} to 1.2 $\times 10^{-7}$ M	0.9947	2.8	[27]

3.3. Mechanism action of ascorbic acid on the oscillating system

The BZ oscillating system has highly complex mechanism due to the involvement of various substances i.e. radicals ions etc. In comparison with conventional BZ-system, the macrocyclic Cu-complex catalyzed BZ oscillator possess some specific features [28] due to the existence of Pi-bond in the ligand (L) in $[CuL](ClO_4)_2$. Such specific features of $[CuL](ClO_4)_2$ includes less activation energy, huge frequency and exposed to exterior perturbation and indorse a higher reaction kinetics including electron donating at each steps in oscillatory reaction.

The FKN mechanism [29,30] is used to explain the mechanistic approach of the macrocyclic Cu-catalyzed BZ system. In particular mechanism, the amount of bromate ion (Br⁻) is responsible for switching on-off the oscillatory reactions. The FKN-mechanism is composed of below 7 oscillatory reactions.

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

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

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

$$BrO_3^- + HBrO_2 + H^+ \leftrightarrow 2BrO_2^\bullet + H_2O \qquad (4)$$

$$Br_2 + HOOCCHOHCH2COOH \rightarrow$$

$$Br^- + H^+ + HOOCCHOHBrCHCOOH \qquad (5)$$

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

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

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

$+ \ BrO_3 \longrightarrow Product$

The first four reactions (1-4) shows the oxidation states of BrO_3^-. The reaction 5 indicate the bromination of malic acid, which usually inhibit as the concentration of Br⁻ is too high into the system. Reaction 6 is the oxidation of $[CuL]^{2+}$ into $[CuL]^{3+}$ by $BrO_2^\bullet$ radical (produced reaction 4. When the amount of $[CuL]^{3+}$ increase, the reaction 7 is take place and produce Br⁻. When the concentration of Br⁻ become high into the system, the reactions from 1 to 4 will initiate again.

In order to confirm the redox reaction of AA with oscillatory reagents or intermediate species, cyclic voltammetry (CV) experiments were performed in the absence and presence of AA in the listed solutions: (a) $H_2SO_4 + NaBrO_3$, (b) $H_2SO_4 + [CuL]^{2+}$, (c) $H_2SO_4 + malic acid$. The CV results confirmed only the redox reaction of AA with BrO_3^- as shown in Fig. 4.

The perturbation of AA (reaction 8) in active B-Z system could greatly affect the reactions 1 and 4 because in both reactions the BrO_3^- was consumed, thus the ΔA was occurred as mention in Fig. 1. The decreased in the amount of BrO_3^- due to the reaction 8, may cause the reduce amount of both $HBrO_2$ (in reaction 1) and $BrO_2^\bullet$ radical (in reaction 4). The decreased amount of $HBrO_2$ is unable to initiate reaction 4 to produce $BrO_2^\bullet$ radical in reaction 4. Such decline in $BrO_2^\bullet$ radical didn't well oxidized $[CuL]^{2+}$ into $[CuL]^{3+}$ via reaction 6. Similarly, the drop in amount of $[CuL]^{3+}$ reduce its reduction to

$[CuL]^{2+}$ in reaction 7. Thus, the decrease in the value of $\log\{[CuL]^{3+}/[CuL]^{2+}\}$ was occur and the change in the oscillation amplitude was noticed.
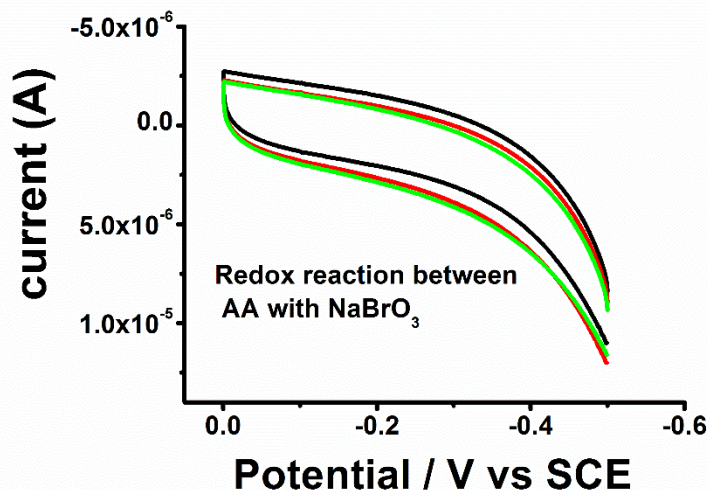

Figure 4. Cyclic voltammograms of $NaBrO_3$ with ascorbic acid; $[NaBrO_3] = 0.01875$ M; Common condition $[H_2SO_4] = 1.00$ M. Scan rate $= 100$ mV /s.

4. CONCLUSIONS

In this article, we successfully demonstrate the determination of ascorbic acid (AA) by using a macrocyclic Cu (II)-complex catalyzed B-Z oscillator. The AA caused ΔA and ΔT which were directly related to its concentration. Thus a linear relationships between the concentrations of AA vs ΔA and ΔT was obtained in its concentration range from 3×10^{-6} M to 1.05×10^{-4} M with correlation coefficients of 0.99 respectively. The cyclic voltammetry results confirmed the redox reaction between BrO_3^- and AA. On the base of oscillation mechanism (FKN), the reaction perturbation mechanism has been proposed.

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