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Quantitative Determination of Kaempferol by using a novel B-Z Chemical Oscillating system Catalyzed by a Cu (II)-tetraazamacrocyclic Complex

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An appropriate analytical technique for determination of kaempferol (KMF) by its perturbation effect on Belousov-Zhabotinskii (B-Z) oscillating system was reported. The macrocyclic copper (II) complex [CuL] $(ClO_4)_2$] was used as a catalyst while malic acid as substrate in B-Z 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 KMF could cause the change in the amplitude of oscillation (ΔA) which was directly related to its concentration (2.5×10^{-6} to 3.0×10^{-4} mol/L) with correlation coefficient of 0.99315. The calculated relative standard deviation (RSD) is 3.1 % by eight samples (1.8×10^{-5} mol/L) and the observed lower limit of detection is 1.25×10^{-6} mol/L. The cyclic voltammetry (CV) experiments were used to confirm the redox reaction between kaempferol and sodium bromate. Furthermore, the reaction perturbation mechanism was derived from the well-known FKN (Field-Koros-Noyes) oscillation mechanism.

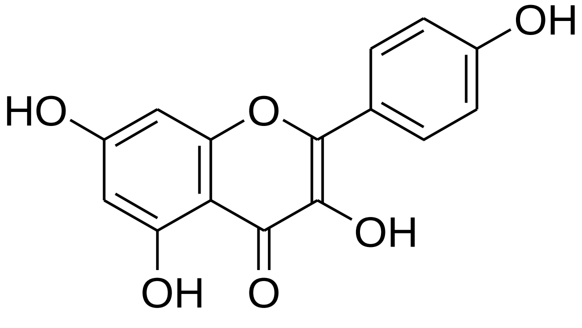
Keywords: Antioxidant; Belousov-Zhabotinskii; Chemical Oscillator; Kaempferol; Oscillation Amplitude

1. INTRODUCTION

Chemical oscillation is a nonlinear phenomenon, which shows continuous change due to the participation of intermediate species. To date, hundreds of chemical oscillators have been reported, such as Belousov-Zhabotinsky (BZ) [1], Bray-Liebhafsky (BL) [2, 3], Briggs-Rauscher (BR) [4-7] and hydrogen peroxide-ferrous cyanide oscillator systems, etc. [8, 9]. The BZ oscillator has been studied in depth. In a particular BZ system, the oxidation of the organic substrate is done with the help of $NaBrO_3$-solution (acidic) in presence of the metal ions, i.e. Ce^{4+}, Mn^{2+}, Ferron Fe $(Phen)_3^{2+}$ and Ru $(biphy)_3^{2+}$ or tetraazamacrocyclic Cu-complex catalyst ($[CuL](ClO_4)_2$). For the first time, Tichonova has used the pulse-perturbation technology (PPT) using oscillation system (BZ) for sample analysis, which has attracted the attention of the world's wise men in the field of quantitative analysis [10, 11].

Among the catalysts used in the BZ system, the cupper catalyst ($[CuL](ClO_4)_2$) can be considered novel catalyst in which the ligand L is 5,7,7,12,14,14-hexamethyl-1,4,8,1,1-tetraazacyclotetradeca-4,11-diene, which has a Pi-bond. This behavior is beneficial to its use as a catalyst for determining compounds in the BZ oscillator. In the BZ oscillator, which is catalyzed by the $[CuL](ClO_4)_2$-Catalyst, the continuous electrons are exchanged between its oxidized $[CuL]^{3+}$ catalyst and reduced $[CuL]^{2+}$ repeatedly. $[CuL]^{2+}$ appeared red color, while $[CuL]^{3+}$ was seemed an orange color. Therefore, the color of the BZ oscillator was expected to exchange between the color of $[CuL]^{2+}$ and $[CuL]^{3+}$, and such experimental data was collected in the PC [8].

Recentally our group has successfully developed macrocyclic Cu-complex catalyzed BZ oscillator for quantitative investagation of alizarin red S [12], calcium pantothenate [13], paracetamol [14], Ag^+ [15], pyrogallol [16], vitamin B6 [17], xylenol orange [18], and catechol [19]. We used BZ oscillating system as instrument for the quantitative determination of kaempferol (KMF, Scheme 1) by its perturbation technique. The influence of KMF replicated as a change in the oscillation amplitude (ΔA), which is linearly relational 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 KMF and sodium bromate. The reaction perturbation mechanism was derivative from the well-known oscillating FKN mechanism.



Scheme 1. Structure of Kaempfrol

2. EXPERIMENTAL

2.1. Reagents

All reagents such as $NaBrO_3$ (National Pharmaceutical Chemical Reagents, China), Alfonate (Aladdin, Shanghai, China), Yamampphenol (Aladdin, Shanghai, China) and Sulphuric Acid (Aldrich 98%) are analytical grade and they do not require additional refining. It is only through the existing literature that the (CuL) $(ClO_4)_2$ has been prepared and characterized by infrared (IR) spectra and elemental analysis. A solution of 0.6 mol/L of sodium bromide, 2.00 mol/L of malic acid, 0.0221 mol/L of $[CuL](ClO_4)_2$ was prepared in 1.00 mol/L of H_2SO_4. Freshly prepare the Kaempfrol solution. Such solution was prepared in 1.00 mol/L H_2SO_4 and then used for perturb oscillations.

2.2. Apparatus

The BZ oscillation setting includes a 50 ml glass container and a potential recording tool. The 50ml glass container is fixed with a temperature-adjuster (thermostat model-DZCS-IIC) to keep the solution temperature at 18 ± 0.5 ˚C. With the help of the 79-3 magnetic mixer (Jiangsu, China), the mixture is standardized at 750 per minute. The Pt electrode (type 213, Shanghai, China) is used as a working electrode, while the saturated calomel electrode (SCE) (type 217, Shanghai, China) is used as a reference electrode. Two electrodes are connected to the PC via Go! Link and amplifiers. The data (potential v.s. time) is analyzed by the logger-lite software. The cycle voltammetry (CV) (CH1660, Shanghai Chenhua Instruments, Ltd, China) was used to carry out the cycle voltammeter.

2.3. Procedure

For BZ oscillating systems, mix 40 ml of oscillatory solution into reaction container in a given order: 1.20 ml of 0.6 mol/L $NaBrO_3$, 28.8 ml of 1.00 mol/L H_2SO_4, 3.8 ml of 2.00 mol/L malic acid solution and 6.2 ml of 0.0221 mol/L cupper complex catalyst $[CuL](ClO_4)_2$. The Pt-electrode and SCE-electrode was inserted into the reaction tank. Both electrodes are connected into PC and record potential changes over time. For the perturbation experiments, different concentrations of Kaempfrol were used to perturb the oscillation cycles. For cycle voltammetry (CV) experiments, the absence of additives Kaempfrol, the acidic solution of each BZ reagent (1.00 ml of 0.6 mol/L sodium bromide + 39 ml of 1.00 mol/L sulphuric acid), (3.8 ml of 2.00 mol/L Malic acid +36.2 ml of 1.00 mol/L sulphuric acid) and (6.2 ml 0.0221 mol/L $[CuL](ClO_4)_2$ + 33.8 ml of sulphuric acid). The total volume for CV experiments was kept at 40 ml by adjusting the volume of sulphuric acid.

3. RESULTS AND DISCUSSION

3.1. Typical oscillation for BZ oscillator

Unperturbed typical oscillation (Figure. 1 a) for BZ system was succeeded by the mixing of the reagents into above order. During the oscillation the periodic changing, the color of the solution from red to orange was noticed, and the below reaction show the continuous changing (redox) reaction in the system. The chemical oscillation shows a repeated difference in the amount of repetitive colors, pH or redox-potential variations, depending on the precise system [24]. For $NaBrO_3$-sulfuric acid-malic acid-$[CuL](ClO_4)_2$, was notice in the form of continuous changing the color.

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

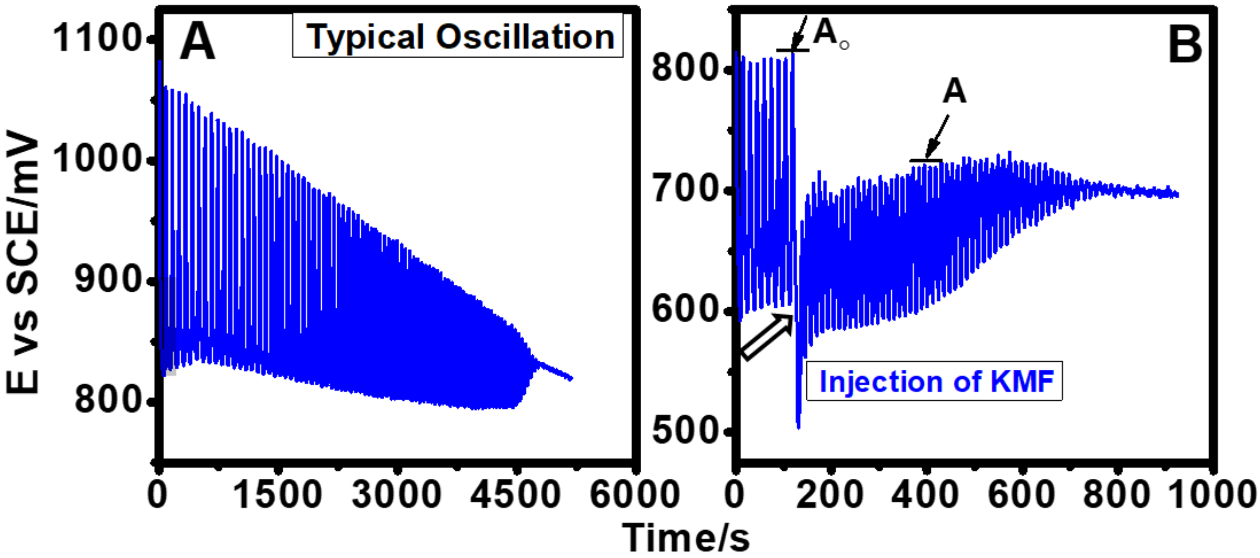


Figure 1. Oscillation profiles for the proposed B-Z oscillator in the absence and presence of kaempferol by the perturbation using Pt vs SCE electrodes, a): [KMF] = 0.000 mol/L; b): [KMF] = 2.25×10^{-5} mol/L; Common condition: $[NaBrO_3] = 1.95\times10^{-2}$ mol/L; [malic acid] = 0.18 mol/L; $[H_2SO_4] = 1.0$ mol/L; $[CuL](ClO_4)_2 = 3.595\times10^{-3}$ mol/L, t = 17 ^{O}C.

3.2. Influence of experimental variables

The oscillation of the chemical system is easily effected by the experimental variables. In order to find the optimum environment for quantitative determination of Kaempfrol (KMF), the influence of the reagents, i.e. $NaBrO_3$, H_2SO_4, malic acid and $[CuL](ClO_4)_2$ catalysts were detected. The optimal value for working conditions is usually measured by three conditions, i.e. (1) the extreme changing of oscillation amplitude (A) to prove the high sensitivity of KMF; (2) A high accuracy are shown due to the perturbation of KMF. (3) Confirmation of the maximum stability of chemical oscillation relative to time, and this property is very important to obtain good results. The influence of precise experimental variables on the BZ system was observed due to the presence and absences of KMF. For the quantitative determination of KMF, $\Delta A = (A_2\text{-}A_1)$ and $\Delta T = (T_2\text{-}T_1)$ are consider as working parameters. Where ΔA of (A_2 and A_1) is the amplitude oscillating before and after injection, respectively [25, 26, 27].

The variation of sulfuric acid concentration of was studied over the range from 0.7 mol/L to 1.4 mol/L. The change was found that as concentration of sulfuric acid increases into the system, the oscillation amplitude (ΔA) decreases first, and increases again at concentration 0.8 mol/L and oscillation amplitude (ΔA) seems increasing up to 1.0 mol/L. From 1.0 mol/L to 1.2 mol/L, the oscillation amplitude (ΔA) again decreases, and oscillation amplitude (ΔA) increases with increase in concentration from 1.2 mol/L to 1.4 mol/L, which is shown in Figure. 2 a. A 1.00 mol/L of sulfuric acid concentration was considered as optimal point, because at this point of concentration the oscillation is more stable.

The effect of malic acid concentration was tested from 0.1 mol/L to 0.2 mol/L. As the amount of malic acid increases into the system, the oscillation amplitude (ΔA) decreases at 0.12 mol/L. The concentration from 0.12 mol/L to 0.16 mol/L, oscillation amplitude (ΔA) of MA increases, and the oscillation amplitude (ΔA) again decreases as shown in Figure 2 b. Thus, a concentration of 0.16 mol/L of malic acid was selected as optimal point.

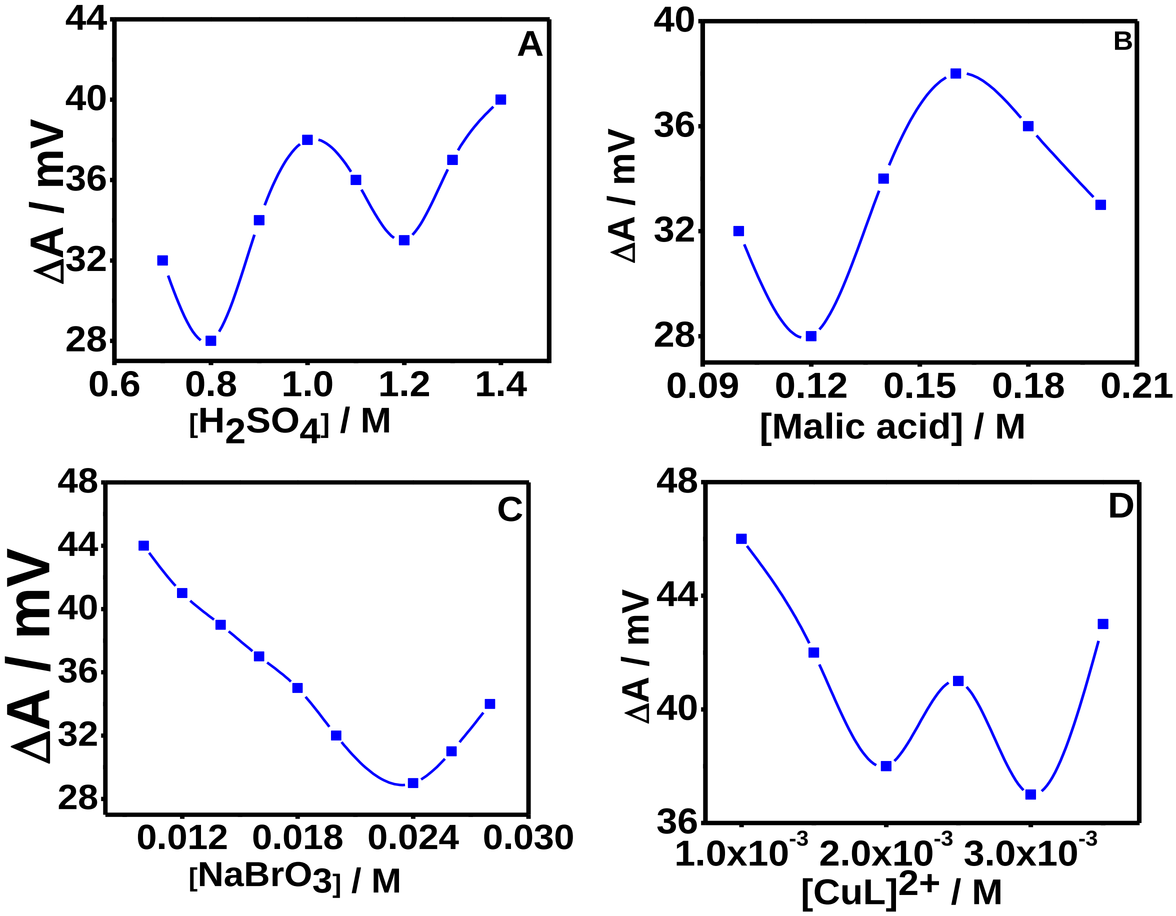


Figure 2. Influence of the concentration (a) sulfuric acid; (b) malic acid; (c) sodium bromate, (d) [CuL]$(ClO_4)_2$ on the kaempferol perturb oscillation system (ΔA= amplitude) Condition: Common condition: T = 17 ^{O}C, [KMF] = 2.25 × 10^{-5} mol/L; (a) [$NaBrO_3$] = 1.95×10^{-2} mol/L; [malic acid] = 0.18 mol/L; [CuL]$(ClO_4)_2$ = 3.595×10^{-3} mol/L; (b) [$NaBrO_3$] = 1.95×10^{-2} mol/L; [H_2SO_4] = 1.0 mol/L; [CuL]$(ClO_4)_2$ = 3.595×10^{-3} mol/L; (c) [malic acid] = 0.18 mol/L; [H_2SO_4] = 1.0 mol/L; [CuL]$(ClO_4)_2$ = 3.595×10^{-3} mol/L; (d) [$NaBrO_3$] = 1.95×10^{-2} mol/L; [malic acid] = 0.18 mol/L; [H_2SO_4] = 1.0 mol/L;

The influence of $NaBrO_3$ concentration was examined from 0.01 mol/L to 0.028 mol/L. It was measured that, by the increasing concentration of $NaBrO_3$ from 0.01 mol/L to 0.024 mol/L, the system is led to decrease in the oscillation amplitude (ΔA). When the concentration was increases from 0.024 mol/L to 0.028 mol/L, oscillation amplitude (ΔA) increases, as mention in Figure 2 c. Thus, finally the concentration 0.024 mol/L for $NaBrO_3$ was selected as optimum concentration for KMF determination.

The $[CuL](ClO_4)_2$ concentration was varied from 0.001 mol/L to 0.0035 mol/L. The oscillation amplitude (ΔA) were incredible effected with increase concentration of $[CuL](ClO_4)_2$ as shown in Figure 2 d. By the increasing the concentration of $[CuL](ClO_4)_2$, oscillation amplitude (ΔA) first decreases and then increases with increasing concentration of $[CuL](ClO_4)_2$ from 0.002 mol/L to 0.0025 mol/L. From 0.0025 mol/L to 0.0035 mol/L, the oscillation amplitude (ΔA) increases with increasing the $[CuL](ClO_4)_2$ catalyst concentration. The concentration of 0.0025 mol/L was chosen as optimal point, because at this concentration the oscillation was uniform.

The complex catalyst $[CuL](ClO_4)_2$-BZ system is highly influence by temperature [27], that is why, the influence of temperature was measured between 15 to 25˚C. We found that, above and below 25˚C, the ΔA was not accurate. Thus, 25˚C was chosen as optimal.

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

Table 1. Influence of foreign ions and species on the quantitative determination of Kaempferol.

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 is simply affected due to the existence of foreign substances. Therefore, the effect of few foreign species was 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 2.25×10^{-5} mol/L KMF was altered as the tolerance limit as indicated in Table 2. 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.

3.3. Quantitative Determination of Kaempferol (KMF)

In the quantitative determination of KMF, different amounts of KMF were used to perturb the BZ system as a result the ΔA was found. We further notice that, as the concentration of KMF into the system increases, the ΔA increases. Thus the lineally proportional curve was achieved between KMF concentration vs ΔA in a concentration range of 2.5×10^{-6} to 3.0×10^{-4} mol/L with correlation coefficient of 0.99315 as shown in Figure. 3. The calibration data was obtained by the following equation:

$$\Delta A = 4.74625 + 132103\,[\text{kaempferol}],\ (r = 0.99315),\ (n = 12)$$

The calculated relative standard deviation (RSD) was obtained by eight measurements of 1.2×10^{-5} mol/L of KMF, which was 3.1 %. The lower limit of detection (LOD) is obtained to be 1.25×10^{-6} mol/L. Such accuracy in the determination of KMF is quite acceptable.

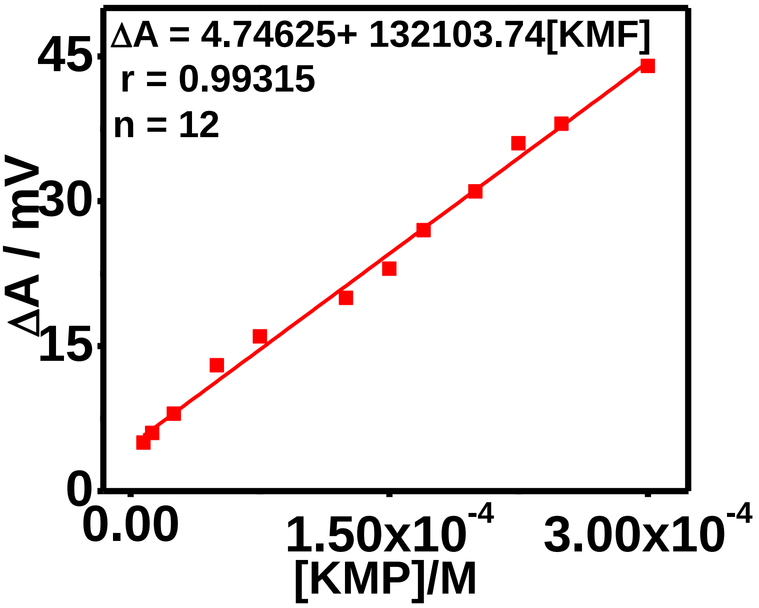


Figure 3. Calibration curve of the change in the in oscillation amplitude vs kaempferol; Common Condition: Concentration range of 2.5×10^{-6} to 3.0×10^{-4} mol/L; Common condition: $[NaBrO_3] = 1.95\times10^{-2}$ mol/L; [malic acid] = 0.18 mol/L; $[H_2SO_4] = 1.0$ mol/L; $[CuL](ClO_4)_2 = 3.595\times10^{-3}$ mol/L, t = 17 ^{O}C.

Table 2. Determination results and recovery for KMF

Sample	Known Concentration / 10^{-5} M	Added Concentration / 10^{-5} M	Found Concentration / 10^{-5} M	Recovery %
1	0.99	0.5	1.352	92.24
2	1.55	0.5	1.716	100.80
3	2.95	1.0	2.245	99.60

4	3.40	2.0	3.081	95.00
5	4.30	2.0	3.880	94.55
6	5.80	2.0	4.792	99.70

Common condition: $[NaBrO_3] = 1.95\times10^{-2}$ mol/L; [malic acid] = 0.18 mol/L; $[H_2SO_4] = 1.0$ mol/L; $[CuL](ClO_4)_2 = 3.595\times10^{-3}$ mol/L, t = 17 ^{O}C.

To check the preciseness of our proposed BZ methodology, the known concentration of KMF was put into the standard liquors (shown in Table 2), and repeated the determination process. The recovery results have shown the accuracy of our proposed method. It lies from 93.70 to 104.00 %, which clearly show that this technique is acceptable for practical analysis. Furthermore, the obtained determination results of KMF by BZ oscillator was indicated in Table 2 and were found that our proposed method is quite accurate and acceptable for the determination of KMF or for other compounds as well.

3.4. Mechanism action of Kaempferol on the oscillating system

BZ oscillation system has a highly complex mechanism due to the involvements of various substances, i.e. free radical ions. Compared with traditional BZ-system, the BZ oscillator catalyzed by the macrocyclic copper complex has some specific characteristics due to the presence of the Pi-bond in the ligand (L) in $[CuL](ClO_4)_2$. Such specific feature of catalyst includes less activation energy [28], great frequency and exposed to exterior perterbation and higher reaction dynamics including each step of the electron in the oscillation reaction. The FKN mechanism is used to explain the mechanism of the BZ system catalyzed by macrocyclic complex. In particular, the amount of bromide ions (Br-) is responsible for the switching (on-off) the oscillation reaction. The FKN mechanism consists of the following 7 oscillating reactions [29, 30].

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

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

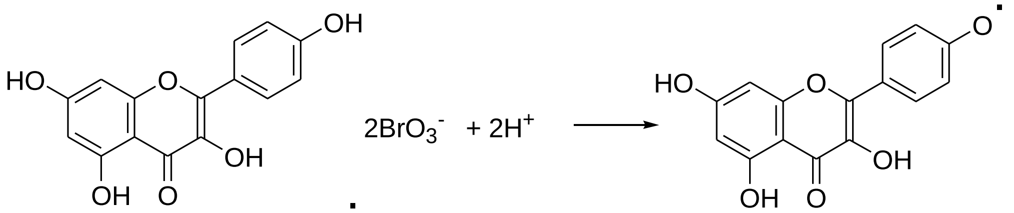
$HOBr + Br^- + H^+ \leftrightarrow Br_2 + H_2O$ (3)

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

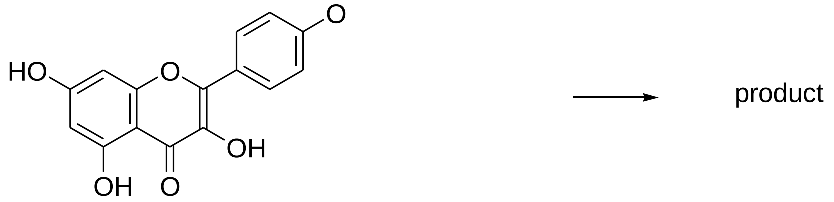
$Br_2 + HOOCCHOHCH_2COOH \rightarrow$
$Br^- + H+ + HOOCCHOHBrCHCOOH$ (5)

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

$HOOCCHOHBrCHCOOH + 6[CuL]^{3+} + 3H_2O \rightarrow$
$6[CuL]^{2+} + Br^- + 2HCOOH + 2CO_2 + 7H^+$ (7)



(8)



(9)

The first four reactions (1-4) show the oxidation states of BrO_3^-. The reaction 5 indicates 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 in reaction 4). When the amount of $[CuL]^{3+}$ increases, the reaction 7 takes place and produces Br^-. When the concentration of Br^- becomes high into the system, the reactions from 1 to 4 will initiate again.

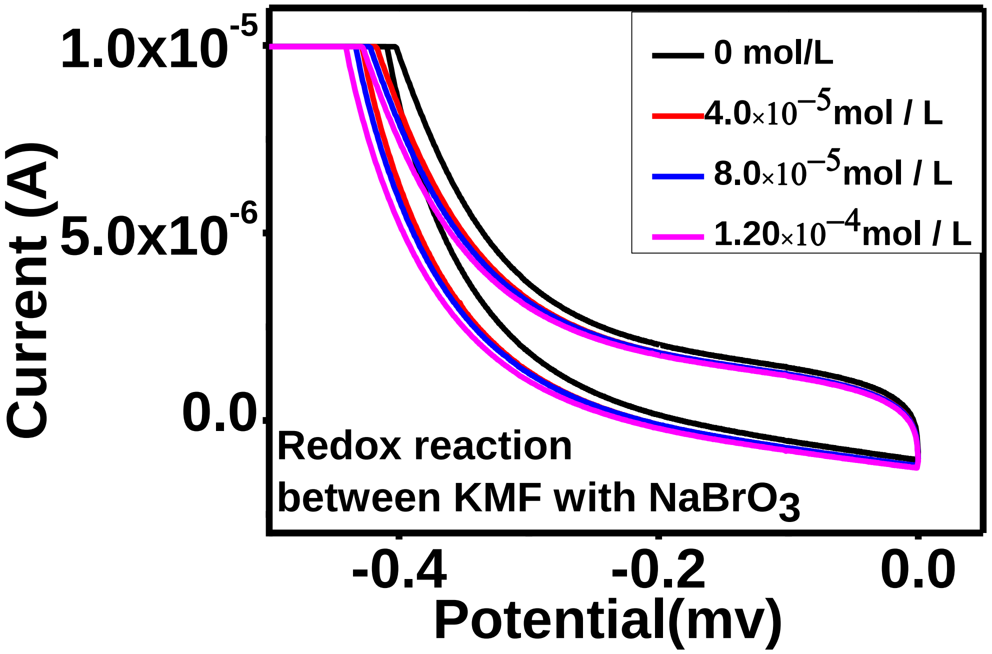


Figure 4. Cyclic voltammograms of $NaBrO_3$ with kaempferol; $[NaBrO_3] = 1.95\times10^{-2}$ mol/L; Common condition $[H_2SO_4] = 1.0$ mol/L. Scan rate = 100 mV /s.

In order to confirm the redox reaction of KMF with oscillatory reagents or intermediate species, cyclic voltammetry (CV) experiments were performed in the absence and presence of KMF in the listed solutions:

(a) $H_2SO_4 + NaBrO_3$, (b) $H_2SO_4 + [CuL]^{2+}$, (c) H_2SO_4 + malic acid.

CV results confirm the redox reaction between KMF and BrO_3^-only. The disturbance of KMF (reaction 8) in the active B-Z system may have a significant impact on reaction 1 and 4, as bromine is consumed in both reactions. A reduction in the amount of bromine-quantity in reaction 8 may result in a decrease in both $HBrO_2$ (in Reaction 1) and BrO_2 free radicals (in Reaction 4). The reduction of $HBrO_2$ cannot trigger reaction 4 to produce BrO_2 free radicals in reaction 4. Thus the decline of the BrO_2 free radical did not oxidize well by reaction 6 similarly, and the drop in the amount of $[CuL]^{3+}$is restored to $[CuL]^{2+}$ in Reaction 7. Therefore, the value of the log $[CuL]^{+3}/[CuL]^{+2}$ decreases to produce a change in the oscillation amplitude.

4. CONCLUSIONS

The suitable technique was used for the quantitative determination of kaempferol (KMF) by using a macrocyclic Cu (II)-complex catalyzed B-Z oscillator. The KMF caused ΔA which were directly related to its concentration. Thus a linear relationship between the concentrations of KMF vs ΔA was obtained in its concentration range from 2.5×10^{-6} to 3.0×10^{-4} M with correlation coefficients of 0.99315 respectively. The cyclic voltammetry results confirmed the redox reaction between BrO_3^- and KMF. On the base of oscillation mechanism (FKN), the reaction perturbation mechanism has been proposed.

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