Scientia Iranica C (2016) 23(6), 2735–2741

SCIENTIA
IRANICA

Sharif University of Technology
Scientia Iranica
Transactions C: Chemistry and Chemical Engineering
www.scientiairanica.com

Research Note

Study of BZ oscillating system in the presence of silica nanoparticles containing NiO using a new approach: Conductometry

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Received 23 September 2014; received in revised form 4 January 2016; accepted 26 September 2016

KEYWORDS
Conductometry;
Oscillating chemical reaction;
BZ oscillating system;
NiO nanoparticles.

Abstract. Oscillating chemical reactions are complex systems involving a large number of chemical species, such as ionic, radical, and molecular intermediates, which exhibit fluctuation in their concentration with time. One of the oscillating chemical reactions is BZ $\{H_2SO_4\text{-}KBrO_3\text{-}CH_2(COOH)_2\text{-}Ce(IV)\}$ system. In this work, for the first time, a new, simple, and appropriate method, i.e. conductometry, was applied to the investigation of BZ oscillating system. Furthermore, presence of SiO_2 nanoparticles containing NiO apparently affected the intensity and period of BZ system. The effect of varying concentration of H_2SO_4, $KBrO_3$, $CH_2(COOH)_2$, and Ce(IV) on the conductance of BZ oscillating chemical system at 20 ($\pm$ 0.1)°C was also investigated. The obtained results of this work indicated that rather than potential and color of the BZ system, the conductance of system also oscillates during the reaction and is also proportional to the reactants concentration as well. The intensity and period of the oscillation are strongly dependent on the concentration of reactants.

1. Introduction

Studies in nonlinear dynamics are part of a rapidly developing interdisciplinary research field. One important investigation area is chemical oscillation reaction [1-4]. Since the publication of Belousov's paper [5] and the proposition of the dissipation structure theory by Prigogine [6], research into oscillating chemical reactions has been developing more rapidly. There has been a focus on the theoretical and experimental chemical kinetics in recent years [3,7]. In these complicated systems of chemical reactions, the concentrations of some reaction intermediates systematically change with time. A well-known oscillating reaction is the BZ reaction which involves oxidation of an organic compound (e.g., malonic acid) by bromate ions in a strongly acidic aqueous medium. This reaction is catalyzed by traces of transition metal ions such as Ce(IV). Zhabotinskii [8] found a linear correlation between the reactant concentration and the period of the BZ reaction and proposed the use of this phenomenon for chemical analysis. Oscillating chemical reactions were also used for the determination of cobalt cation [9] and antioxidant activity of natural phenolic compounds [10]. Several studies have also been performed illustrating the possibility of analytical applications of regular chemical oscillations [11-14]. Particularly, a procedure was reported to determine various compounds using copper (II) catalyzed oscillating chemical reaction between hydrogen peroxide

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and sodium thiocyanate in alkaline medium [15-17]. Recently, Samadi and co-workers have reported investigation of copper(II) catalyzed oscillating chemical reaction between hydrogen peroxide and sodium thiocyanate in alkaline medium using conductometry and determine the cysteine and methionine by this technique [18,19].

For the first time, this work focuses on the study of BZ oscillating system, i.e. H_2SO_4-$KBrO_3$-$CH_2(COOH)_2$-Ce(IV), in a batch reactor at a constant temperature of 20 (± 0.1)°C using a new method, i.e. conductometry. The behavior of oscillating system was investigated by changing one of the reactants, while the other ingredients are constant.

2. Experimental

2.1. *Materials and methods*

All chemical compounds were purchased from Merck Company and were used without further purification.

In a typical synthesis of NiO/SiO_2, Cetyltrimethylammonium bromide (CTAB) was dissolved in an appropriate amount of deionized water, and then NaOH was added to this solution followed by stirring (at 500 rpm) for 15 minutes to obtain a clear solution. Then, an appropriate amount of $Ni(NO_3)_2$ was added to this solution. After that, tetraethyl orthosilicate (TEOS) was added to this solution under stirring. The obtained suspension was stirred for further 5 hours, and then was transferred into the Teflon-lined stainless steel and autoclaved at 353 K for 72 hours. The brownish precipitate was filtered and washed with sufficient amount of deionized water and dried at 373 K overnight. The synthesized samples calcined at 823 K under air for 6 hours with a heating rate of 5 K/min from room temperature to 823 K. The final molar composition of reactants was 1.0 TEOS, 0.15 CTAB, 300 H_2O, 0.1 NaOH and 0.1 $Ni(NO_3)_2$.

For the investigation of BZ oscillating chemical reaction, stock solutions were prepared from commercially available analytical-grade (MERCK) standard solutions. Doubly distilled water was used throughout for preparation of solutions. In each series of experiments, the concentration of one reactant was varied, while holding the others constant. The temperature was maintained at 20 (± 0.1)°C. The oscillating reaction was carried out in water-jacketed cover in a batch system. In a reaction vessel, 2 mL of H_2SO_4 (0.8 mol L^{-1}), 1 mL of $KBrO_3$ (0.2 mol L^{-1}), and 1 mL of Malonic acid (0.5 mol L^{-1}) were added and mixed with magnetic stirring. Oscillating reaction was started by adding 0.2 mL of Ce(IV) (0.04 mol L^{-1}) to the reaction vessel. The conductance of reaction solution was recorded over 600 seconds and at interval time of 0.1 second.

2.2. *Apparatus*

X-Ray Diffraction (XRD) patterns were recorded on a Seifert TT 3000 diffractometer using Cu Kα radiation of wavelength 0.15405 nm. Diffraction data were recorded in the region of 30−60° 2θ at an interval 0.01° 2θ. A scanning rate of 1.0° 2θ/min was used. Scanning electron micrographs were recorded using a Zeiss DSM 962 (Zeiss, Oberkochen, Germany). Samples were deposited on a sample holder with an adhesive carbon foil and sputtered with gold. The conductograms were recorded with a computer-controlled Jenway 4020 conductometer in kinetic mode. All measurements were carried out in a batch system at constant temperature of 20 (± 0.1)°C.

3. Results and discussion

SEM image of calcined NiO/SiO_2 nanoparticles is illustrated in Figure 1. As can be seen, the NiO/SiO_2 nanoparticles are in nanometer range and have a semi-spherical shape.

High angle XRD patterns of calcined NiO/SiO_2 nanoparticles are presented in Figure 2. The small

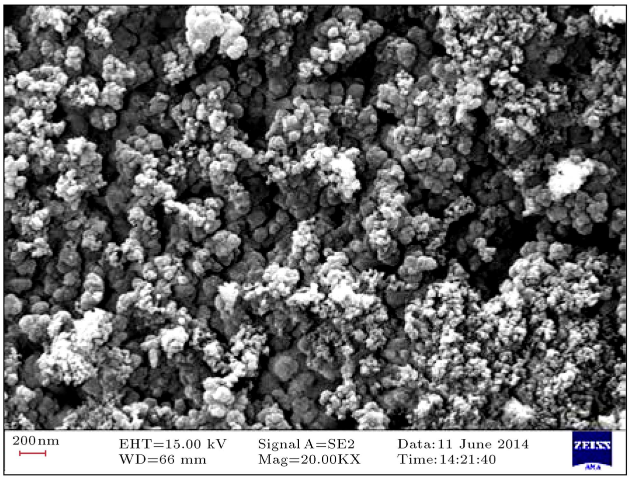

Figure 1. SEM image of NiO/SiO_2 nanoparticles.

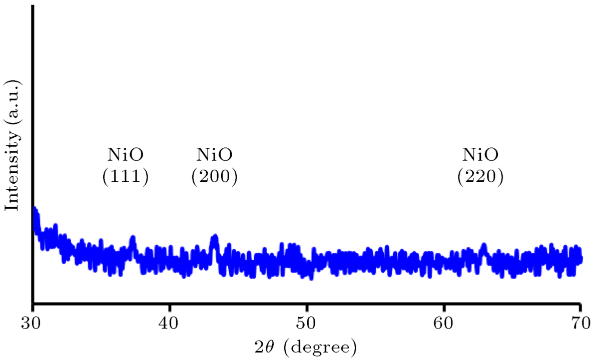

Figure 2. High angle XRD pattern of NiO/SiO_2 nanoparticles. The numbers in parentheses correspond to the miller indices of nickel oxide.

peaks at high angle XRD pattern, which are indexed as (111), (200), and (220) can be related to the presence of nickel oxide in the calcined sample.

According to the Oregonator model, BZ reaction includes three steps:

A. Non-radical, two-electron step;

B. Radical, one-electron step;

C. A delayed negative feedback loop step.

In step A, Br^- is a critical intermediate and Ce(III) is present at high concentration. $[Br^-]$ is consumed, but Ce(III) remains intact. In step B, concentration of $HBrO_2$ is high and Ce(III) oxidizes to Ce(IV). In step C, Ce(IV) is reduced to Ce(III) and the oscillation cycle is completed.

In other words, the reaction between bromate and malonic acid in acidic medium is catalyzed by Ce(IV).This reaction is described by the Oregonator model [3] in three steps as follows:

- **Step A**: Non-radical step (high concentration of Br^- ion, two electrons):

$$W + Y \rightarrow X + P, \tag{1}$$

$$X + Y \rightarrow 2X + 2Z. \tag{2}$$

- **Step B:** Radical set (low concentration of Br^- ion, high concentration of free radicals, one electron):

$$X + Y \rightarrow 2P, \tag{3}$$

$$X + X \rightarrow W + P. \tag{4}$$

- **Step C:** Completes the oscillating reaction by regenerating the start up conditions through reducing the Ce(IV) to Ce(III) and the production of bromine ions:

$$Z \rightarrow fY. \tag{5}$$

In this model, $W = [BrO_3^-]$, $X = [HBrO_2]$, $Y = [Br^-]$, $P = [HBrO]$, and $Z =$ Ce(IV).

The net effect of Step A is the removal of $[Br^-]$ and generation of $BrCH(COOH)_2$. Step A leads to Step B by the consumption of $[Br^-]$. For the oscillation to occur, there must be a wat to turn off Step B by reducing Ce(IV) back to Ce(III), i.e. to return control to Step A and to reset the system. This is carried out by Step C, whose function (after a delay) is to produce $[Br^-]$ while Ce(IV) is accumulated with [HOBr], and it completes with a negative-feedback loop. Also, Step C reduces Ce(IV) back to Ce(III) to reinitialize Step B for the next oscillation.

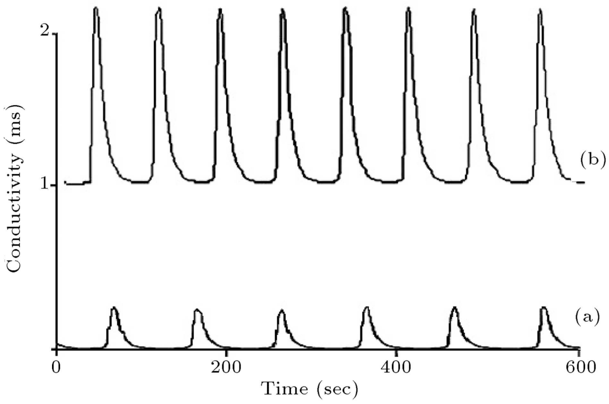

Figure 3. A typical conductograms of the H_2SO_4-$KBrO_3$-$CH_2(COOH)_2$-Ce(IV) oscillating system with final concentration of H_2SO_4 (0.3810), $KBrO_3$ (0.0476), $CH_2(COOH)_2$ (0.1190), and Ce(IV) (1.9×10^{-3}): (a) In the absence, and (b) in the presence of NiO/SiO_2 nanoparticles.

Figure 3 shows the temporal evolution of oscillating reaction in the system of H_2SO_4-$KBrO_3$-$CH_2(COOH)_2$-Ce(IV) with the final concentration of H_2SO_4 (0.381 M), $KBrO_3$ (0.0476 M), $CH_2(COOH)_2$ (0.1190 M), and Ce(IV) (1.9×10^{-3} M) without (Figure 3(a)) and with the addition of 0.1 gram of NiO/SiO_2 nanoparticles (Figure 3(b)). The oscillating behavior is the same as reported with the electrochemical methods [20,21]. However, the presence of NiO/SiO_2 nanoparticles had a considerable effect on the BZ oscillating reaction and increased the intensity of oscillations together with decreasing their period. Increase of intensity of oscillation in the presence of NiO/SiO_2 nanoparticles can be related to the increase of oxidation rate of Ce(III) to Ce(IV), i.e. one-electron step. On the other hand, decreasing the period of oscillation in the presence of NiO/SiO_2 nanoparticles can be attributed to the fast consumption of Br^- during Step A (two-electron step). Hereafter, due to these effects, NiO/SiO_2 nanoparticles were used in all the experiments.

3.1. The effect of H_2SO_4 concentration

The influence of H_2SO_4 on the conductance of BZ oscillating system was investigated in a series of experiments with different concentrations of H_2SO_4 and constant concentration of the other reagents. The experiment was performed with the final constant concentrations of $KBrO_3$, 0.0476 M, $CH_2(COOH)_2$, 0.1190 M, and Ce(IV) 1.9×10^{-3} together with different H_2SO_4 concentrations of 0.179, 0.268, 0.358, 0.446, 0.536, 0.624, and 0.714 M. Figure 4 illustrates the conductograms of the corresponding solutions. All spectra were recorded in the kinetic mode with the same instrumental conditions (Figure 4). Results obtained from these experiments revealed that by increasing H_2SO_4 concentration, the period of the oscillating system decreases. But, increase of intensity of oscillation is more apparent (Figure 5). According

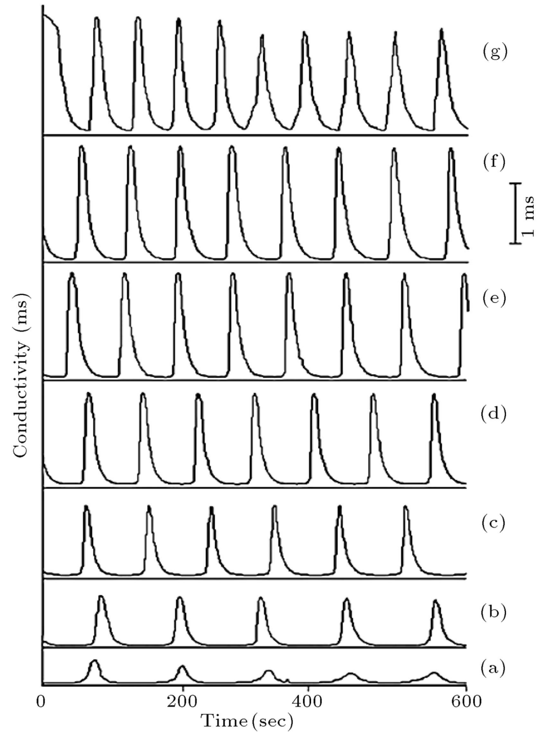

Figure 4. Conductograms of the H_2SO_4-$KBrO_3$-$CH_2(COOH)_2$-Ce(IV) oscillating system at different H_2SO_4 concentrations: (a) 0.179, (b) 0.268, (c) 0.358, (d) 0.446, (e) 0.536, (f) 0.624, and (g) 0.714 M and constant concentration of $KBrO_3$, 0.0476 M; $CH_2(COOH)_2$, 0.1190 M; and Ce(IV), 1.9×10^{-3} M.

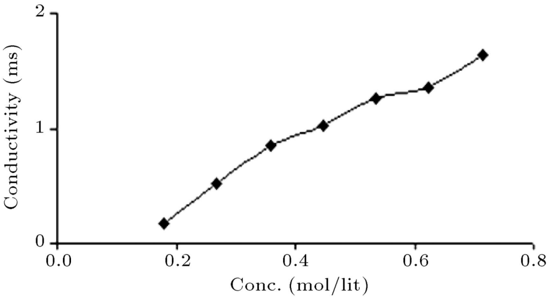

Figure 5. The variation of absorbance with the concentration of H_2SO_4 in H_2SO_4-$KBrO_3$-$CH_2(COOH)_2$-Ce(IV) oscillating system.

to Oregonator model, it can be said that the increase of acid concentration increases the rate of Step B which leads to the higher intensity of oscillations.

3.2. The effect of $KBrO_3$ concentration

The effect of the $KBrO_3$ was assessed with different concentrations of $KBrO_3$ (0.0190, 0.0380, 0.0571, 0.0761, and 0.0951 M), and constant concentration of H_2SO_4, 0.381 $CH_2(COOH)_2$, 0.1190, and Ce(IV), 1.9×10^{-3} M. The oscillations of the corresponding solutions are shown in Figure 6. As can be seen, changing the concentration of $KBrO_3$ influenced mainly the period rather than the intensity of the oscillating system.

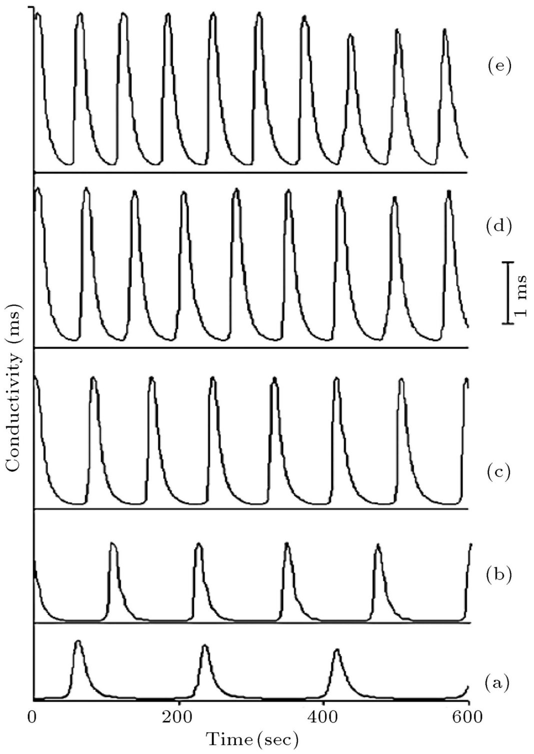

Figure 6. Conductograms of the H_2SO_4-$KBrO_3$-$CH_2(COOH)_2$-Ce(IV) oscillating system at different $KBrO_3$ concentrations: (a) 0.0190, (b) 0.0380, (c) 0.0571, (d) 0.0761, and (e) 0.0951 M, and constant concentration of H_2SO_4, 0.381 M; $CH_2(COOH)_2$, 0.1190 M; and Ce(IV), 1.9×10^{-3} M.

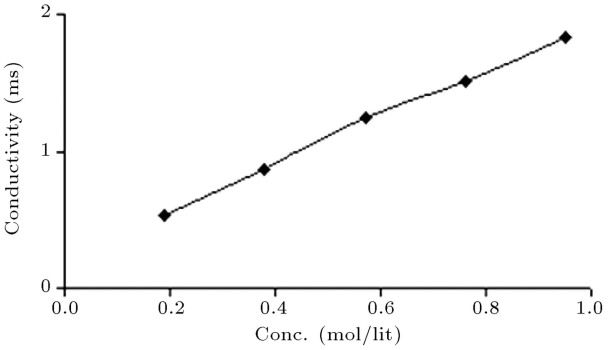

Figure 7. The variation of conductance with the concentration of $KBrO_3$ in H_2SO_4-$KBrO_3$-$CH_2(COOH)_2$-Ce(IV) oscillating system.

According to this result, it can be deduced that Step A proceeds faster than Step B. The obtained results reveal that the conductance of the system is linear with $KBrO_3$ concentration (Figure 7).

3.3. The effect of Malonic acid concentration

In these series of experiments, the concentration of malonic acid was varied between 0.0476 M and 0.1905 M with constant concentration of H_2SO_4, 0.3810 M; $KBrO_3$, 0.0476 M; and Ce(IV), 1.9×10^{-3}. Figure 8 displays the conductograms of the BZ oscillating sys-

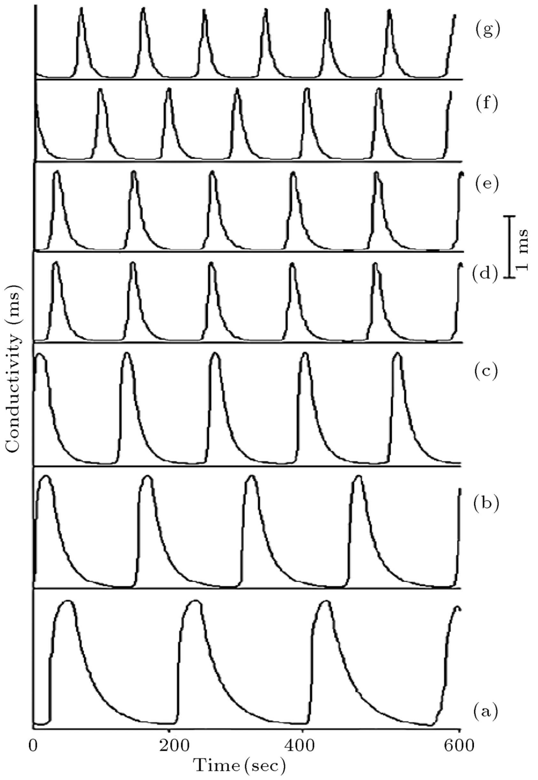

Figure 8. Conductograms of the H_2SO_4-$KBrO_3$-$CH_2(COOH)_2$-Ce(IV) oscillating system at different $CH_2(COOH)_2$ concentrations: (a) 0.0476, (b) 0.0714, (c) 0.0952, (d) 0.119, (e) 0.1429, (f) 0.1667, and (g) 0.1905 M, and constant concentration of H_2SO_4, 0.381 M; $KBrO_3$, 0.0476 M; and Ce(IV) 1.9×10^{-3} M.

tem with different concentrations of malonic acid. As can be seen, the oscillating behavior is also affected by the concentration of malonic acid. As the concentration of malonic acid increases, both the intensity and period of the oscillating system decrease. This behavior might be attributed to the simultaneous increase of reaction rate of Steps C and A, respectively. This suggestion can be related to the fact that upon Oregonator model, malonic acid is consumed during these two steps. The relationship of the intensity of the oscillation signal with concentration of malonic acid is shown in Figure 9.

3.4. The effect of Ce(IV) concentration

Figure 10 shows the conductograms of BZ oscillating system at different concentrations of Ce(IV): (a) 9×10^{-4}, (b) 1.4×10^{-3}, (c) 1.9×10^{-3}, (d) 2.4×10^{-3}, (e) 2.9×10^{-3} M, and at constant concentrations of H_2SO_4, 0.381 M; $KBrO_3$, 0.0476; and $CH_2(COOH)_2$, 0.1190 M. As can be seen, by increasing the concentration of Ce(IV), the intensity of signal (conductance of system) is increased (Figure 11). However, the results indicated that the period of oscillation is prolonged by increasing the Ce(IV) concentration. On the basis of previous reports [3] and according to the Oregonator model, these observations can be attributed to Steps B and C, respectively (Eqs. (3)-(5)). In other words, by increasing Ce(IV) concentration, the time for the feedback is delayed; hence, the period of oscillation increases (Figure 11). In this way, Step B becomes predominant and higher amounts of [Br^-] are produced during Step C.

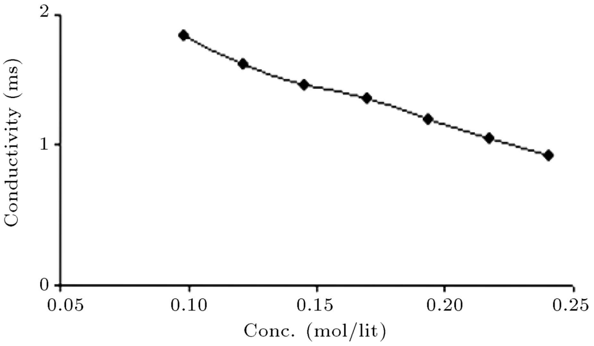

Figure 9. The variation of conductance with the concentration of malonic acid in H_2SO_4-$KBrO_3$-$CH_2(COOH)_2$-Ce(IV) oscillating system.

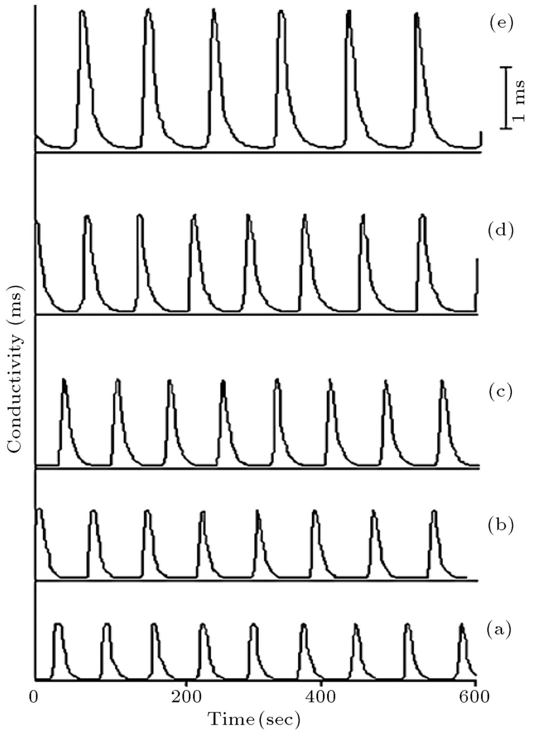

Figure 10. Conductograms of the H_2SO_4-$KBrO_3$-$CH_2(COOH)_2$-Ce(IV) oscillating system at different Ce(IV) concentrations: (a) 9×10^{-4}, (b) 1.4×10^{-3}, (c) 1.9×10^{-3}, (d) 2.4×10^{-3}, and (e) 2.9×10^{-3} M, and constant concentration of H_2SO_4, 0.381 M; $KBrO_3$, 0.0476 M; and $CH_2(COOH)_2$, 0.1190 M.

4. Conclusion

For the first time, The present work presents the application of a very simple and applicable method, i.e. conductometry, for investigation of the oscillating

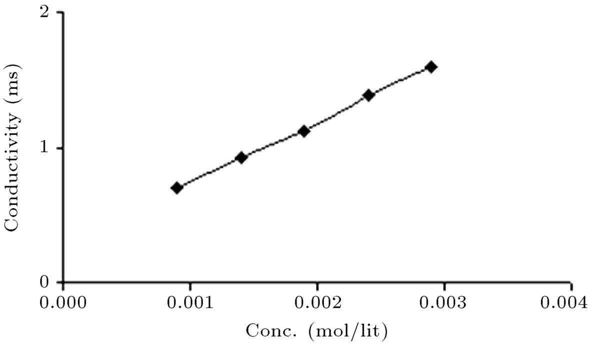

Figure 11. The variation of conductance with the concentration of Ce(IV) in H_2SO_4-$KBrO_3$-$CH_2(COOH)_2$-Ce(IV) oscillating system.

system of H_2SO_4-$KBrO_3$-$CH_2(COOH)_2$-Ce(IV). The species of BZ oscillating system are responsible for the variation of conductance of system which is oscillated with time during the reaction. The intensity and period of the BZ oscillating system are influenced, in terms of conductivity, by changing the ingredients of concentration as well as the presence of NiO/SiO_2. The results reveal that there is a linear relationship between the conductance signal and reactants concentration.

Acknowledgement

The authors are grateful to Mr. Mahdi Delshad for performing conductometric measurements.

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