Dynamics of oscillating Belousov-Zhabotinsky reaction in the presence of ethanol

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Abstract

We present a study of the effect of ethanol on the dynamics of the oscillating ferroin-catalyzed Belousov-Zhabotinsky (BZ) reaction, an oxidation of malonic acid by an acidified bromate. The color of the well-stirred BZ solution alternately changes between red and blue, corresponding to the reduced ($Fe(o\text{-}phen)_3^{2+}$) and oxidized ($Fe(o\text{-}phen)_3^{3+}$) states of the catalyst, respectively. The changes in color occur with a specific period. The dynamics of the oscillation are accelerated when small portion of ethanol is added. The period and amplitude of the oscillation decrease when the concentration of ethanol is increased. When the ethanol concentration reaches a threshold, the oscillation is stopped, and the solution stays blue, which correspond to the oxidized states of the catalyst. Unlike the conventional BZ reaction, NaBr is not added in our BZ preparation so the production of toxic bromine vapors is avoided. Therefore, the presented BZ reaction might serve as a quick and safe system for measuring the ethanol concentration in, e.g., beverage and food industries.

Keywords: *Belousov-Zhabotinsky reaction, Oscillation period, Ethanol.*

1. Introduction

The Belousov–Zhabotinsky (BZ) reaction is an oxidation of an organic compound, such as malonic acid by an acidified bromate (Winfree, 1984). Thin layers of an excitable BZ reaction often exhibit propagating concentration waves in forms of spiral waves (Winfree, 1972; Müller, Plesser, & Hess, 1985) so they are widely used as model systems to study wave dynamics in excitable media (Swinney & Krinsky, 1991; Kapral & Showalter, 1995). For different initial concentration of reagents, the color of well-stirred BZ solutions oscillates in time (Field, 1972). When ferroin is used as the catalyst, the BZ color switches between red and blue, which correspond to the reduced ($Fe(o\text{-}phen)_3^{2+}$) and oxidized ($Fe(o\text{-}phen)_3^{3+}$) states of the catalyst.

Ethanol or ethyl alcohol is a volatile, flammable, colorless liquid with a slight characteristic odor. It can be naturally produced by the fermentation of sugars by yeasts or via petrochemical processes. Ethanol is utilized in many applications, for instance, cosmetics and beauty products, household products, food additives, alcoholic beverages, and fuel (Chemical safety facts, n.d.). The concentration of ethanol in the products is very important, and it is measured by using different tools and methods as mentioned in (Somboon & Sansuk, 2018; Sansuk, Tongphoothorn, Sirimungkala, & Somboon, 2019).

Recently, a precise and inexpensive method for determination of ethanol in gasohol samples was demonstrated using the colorimetric oscillating pattern of a widely used version of the ferroin-catalyzed BZ reaction where NaBr was used as a reagent (Sansuk et al., 2019). Using such recipe, the toxic bromine, whose vapors irritate eyes and throat (Lenntech, n.d.), are produced after NaBr is added into the mixture. Ones must wait for a few minutes until the orange-brown solution becomes clear (after the bromine evaporation). Finally, ferroin can be added to complete the BZ reaction.

In this work, we present a study of the effect of ethanol on the oscillation of another version of ferroin-catalyzed BZ reaction in the absence of the bromine production. The preparation of the BZ reaction can be performed quicker and safer. Therefore, this study may be used as a quick and safe method for measuring the ethanol concentration in, e.g., beverage and food products.

2. Objectives

1. To study dynamics of Belousov – Zhabotinshy reaction.
2. To study the effects of ethanol on dynamic of Belousov – Zhabotinsky reaction.

3. Materials and Methods

In this work, the BZ reaction was prepared using sodium bromate ($NaBrO_3$), sulfuric acid (H_2SO_4), malonic acid ($CH_2(COOH)_2$) and ferroin ($Fe(o\text{-}phen)_3SO_4$). All reagents were the highest commercially available grade and purchased from Merck. Stock solutions of $NaBrO_3$ (1 M) and $CH_2(COOH)_2$ (1 M) were prepared by dissolving powder in deionized water (conductivity ~ 0.056 µS cm^{-1}), whereas solutions of H_2SO_4 (2.5 M) and ferroin (25 mM) from Merck were used without further preparation. For each experiment, appropriate volumes of all stock solutions were mixed and diluted in deionized water to obtain a BZ solution. In a 10-ml transparent volumetric flask, we mixed 2 ml of H_2SO_4, 0.5 ml of $NaBrO_3$, 0.5 ml of $CH_2(COOH)_2$, 0.2 ml of ferroin, and 6.8 ml of deionized water so the initial concentration of 10 ml of the BZ solution were 500 mM H_2SO_4, 50 mM $NaBrO_3$, 50 mM $CH_2(COOH)_2$, and 0.5 mM ferroin. The effect of ethanol (C_2H_6O) on the BZ reaction was studied by adding planed volume of 99.5% ethanol to the BZ reaction.

To investigate the temporal dynamics of the reaction, the BZ solution with a volume of 10 ml in the transparent volumetric flask was well-stirred. The flask was placed between a white light source and a color CCD camera (Wisenet HCB-6000). In each experiment, the BZ reaction was observed and recorded as a video file for about 40 minutes. The room temperature was controlled to 25±1 ℃.

During the experiments, the color of the BZ solution changed between red and blue, corresponding to reduced and oxidized states of the catalyst, as shown in Figure 1. To analyze the dynamics of the BZ reaction, a series of images with 1-s delay time between images was extracted from the video file. Then, the color images were converted to grayscale images with a resolution of 8 bits. Therefore, the red and blue pixels in the original images corresponded to low and high gray levels, respectively. To analyze the gray level which changes in time, the gray level of a rectangle of two hundred pixels in the images was averaged and taken as the intensity, which was followed in the course of time, as shown in Figure 1. The interval between two peaks of the intensity was measured as the oscillation period T.

4. Results and Discussion

Figure 1 shows example images of the BZ solution in the absence of ethanol and the corresponding image intensity. The red and blue colors of the solution, due to the reduced ($Fe(o\text{-}phen)_3^{2+}$) and oxidized ($Fe(o\text{-}phen)_3^{3+}$) states of the ferroin catalyst, corresponded to the low and high intensity levels of about 95.9 and 114.3, respectively, so the amplitude of the oscillation was about 114.3 – 95.9 = 18.4 gray levels. The oscillation period was about 117 s.

Figure 2 shows the image intensity over time of the BZ solutions with different concentration of ethanol. When the percentage (%v/v) of ethanol in the solutions is increased, it can be clearly seen that the intensity oscillated with shorter period (shorter interval between two peaks). Furthermore, the oscillation amplitude was also decreased.

The detail of the effect of ethanol on both the oscillation period and the oscillation amplitude is summarized in Table 1. The oscillation period monotonously decreased when the solution contained more ethanol. Furthermore, we show that ethanol also decreased the amplitude of oscillation. Finally, the oscillation disappeared, and the solution remained in blue color (corresponding to the oxidized state of the ferroin catalyst) when the percentage of ethanol reached 0.9%v/v.

Our results about the oscillation of the BZ color in time (in Figure 1) and the effect of ethanol of the period (in Table 1) are similar to those reported earlier for the BZ reaction containing NaBr as a reagent (Sansuk et al., 2019). However, we did not add NaBr in our BZ reaction, so the toxic bromine vapors did not appear during the solution preparation. Therefore, the preparation of the BZ solutions in this study was easier and quicker.

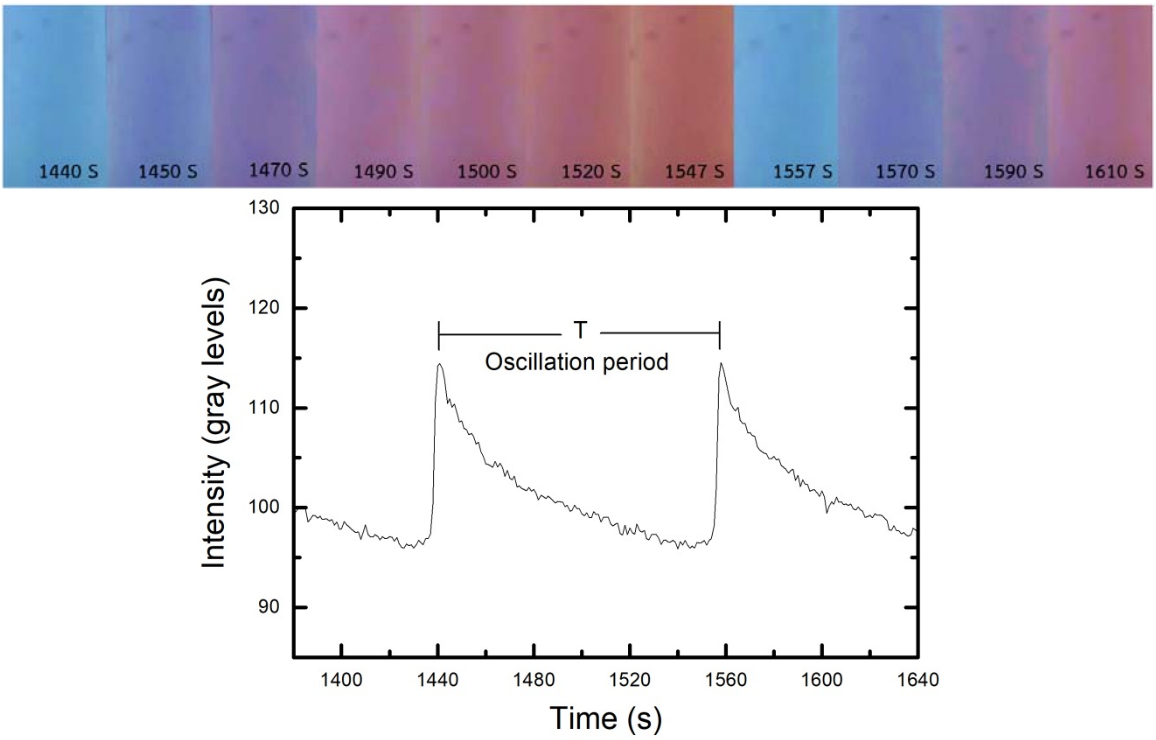

Figure 1 (top) Example color images of the BZ reaction at different time and (bottom) the intensity over time

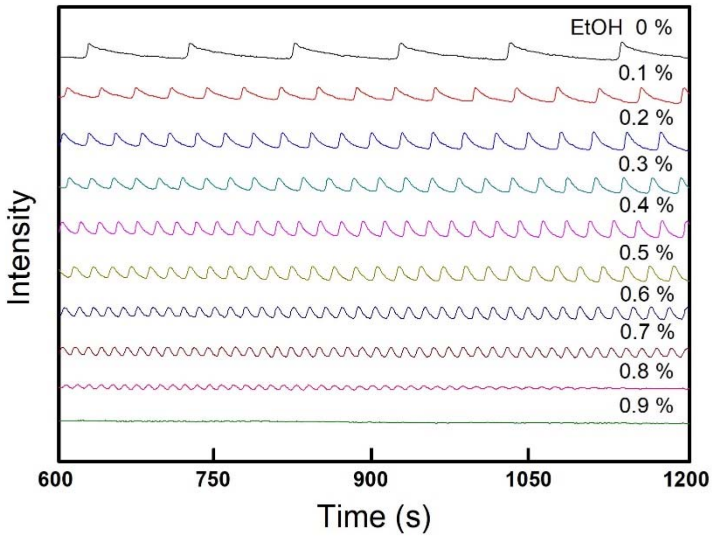

Figure 2 Oscillation of image intensity of the BZ solution containing different percentage of ethanol up to 0.9%v/v

Table 1 Period T and amplitude A of the BZ oscillation at different percentage of ethanol

Ethanol (%v/v)	Period (s)	Amplitude (gray level)
0	117	18.4
0.1	44	20.6
0.2	35	20.4
0.3	29	19.4
0.4	29	17.4
0.5	25	15.6
0.6	19	12.4
0.7	15	9.2
0.8	11	5.7

5. Conclusion

We have presented an investigation of the ethanol effect on the oscillation of the BZ reaction where NaBr was not used in the ingredient, so the toxic bromine was not produced. Both period and amplitude of the oscillation in color of the solution between red and blue, due to the reduced and oxidized states of the catalyst, decreased when the concentration of ethanol was increased. The oscillation was stopped, and the solution stayed in blue (the oxidized state of ferroin) when the ethanol concentration reached a threshold. Since the toxic bromine is not produced in the solution preparation, we suggest utilizing this BZ reaction as a quick and safe method for measuring the ethanol concentration in beverage and food industries.

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