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Electrochemical examination of the pyrocatechol influence on the Bray-Liebhafsky reaction after the oscillatory period

Elektrohemijsko ispitivanje uticaja pirokatehola na Bray-Liebhafsky reakciju nakon oscilatornog perioda

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Abstract

Thanks to the great sensitivity of oscillating reactions to external perturbations, which primarily refers to different analyte addition, chemical oscillators have become very popular for analytic determination of "reactive" analytes, and thus expand their use to many areas, such as environmental, pharmacy, food science etc. This paper aims at an electrochemical examination of the pyrocatechol (analyte) influence on the Bray-Liebhafsky (BL) reaction after the oscillatory period, precisely after six regular oscillations. Pyrocatechol addition provokes the appearance of one more BL oscillation after the second induction period. For investigated BL system, in a range of pyrocatechol concentrations from 2.7 × 10^{-6} M to 1.2 × 10^{-4} M, the period between sixth and seventh oscillations shows linear dependence with added pyrocatechol concentration. The obtained regression equation can be a useful tool for analytical purposes and accordingly, potential determination of unknown pyrocatechol concentration.

Keywords: *Bray-Liebhafsky reaction; oscillatory reaction; pyrocatechol; electrochemical measurements, environmental protection*

Izvod

Zahvaljujući velikoj osetljivosti oscilatornih reakcija na spoljne perturbatore, koja se prvenstveno odnosi na dodavanje različitih analita, hemijski oscilatori postali su vrlo popularni za analitičko određivanje „reaktivnih" analita, proširivši svoju primenu na mnoge naučne grane, poput zaštite zivotne sredine, farmacije, nauke o hrani itd. Ovaj rad ima za cilj elektrohemijsko ispitivanje uticaja pirokatehola (analita) na Bray-Liebhafsky (BL) reakciju nakon oscilatornog perioda, odnosno nakon šest pravilnih oscilacija. Dodatak pirokatehola izaziva pojavu još jedne BL oscilacije nakon drugog indukcionog perioda. Za ispitivani BL sistem, u opsegu koncentracija pirokatehola od 2,7 × 10^{-6} M do 1,2 × 10^{-4} M, period između šeste i sedme oscilacije pokazuje linearnu zavisnost od koncentracije dodatog pirokatehola. Dobijena kalibraciona jednačina se može koristiti u analitičke svrhe i shodno tome, za potencijalno određivanje nepoznate koncentracije pirokatehola.

Ključne reči: *Bray-Liebhafsky reakcija, Oscilatorna reakcija, pirokatehol, elektrohemijska merenja, zastita životne sredine*

Introduction

Bray-Liebhafsky (BL) reaction is the oldest known oscillating reaction [1]. Since it was discovered, the BL system has attracted the high interest of nonlinear scientists [2,3]. The BL reaction represents the catalytic decomposition of the hydrogen-peroxide into oxygen and water, in the presence of potassium iodate, KIO_3^- and hydrogen ions, H^+:

$$2\ H_2O_2 \rightarrow 2\ H_2O + O_2 \quad (1)$$

Although it seems simple, since it includes only three chemical species (iodate, hydrogen-peroxide, and usually sulfuric or perchloric acid), the Bray-Liebhafsky reaction is very complex and takes place via several intermediates, radical or non-radical [2-6]. By monitoring the concentrations of some intermediates, it was found that they periodically increase and decrease over time at regular intervals synchronous with periodic changes in the rate of oxygen gas release [7]. The concentrations of reactants and products during the oscillatory reaction do not oscillate, but a change in a cascade, reflecting periodic changes in the rates of their disappearance (reactants), ie. formation (products).

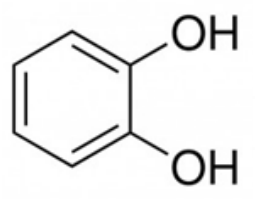

Figure 1. *The structural formula of the chemical compound pyrocatechol*

Thanks to the great sensitivity of oscillating reactions to external perturbations, which primarily refers to different analyte addition, chemical oscillators have also become very popular for analytic determination of "reactive" analytes, usually antioxidant or radical scavengers [8,9]. The influence of pyrocatechol as an analyte (see Figure 1.), was already examined in the Briggs-Rauscher reaction by Cervellati and coworkers [10], as well as in the Bray-Liebhafsky reaction by Maksimović and coworkers [11]. Pyrocatechol (1,2-dihydroxybenzene) finds its wide application in the agricultural and food industry, but also in the production of pesticides, cosmetics, and paints, which results in a frequent need for its determination [12]. However, in both oscillating systems pyrocatechol was added in the oscillatory regime of appropriate reactions. Thus, the main idea of this paper is an electrochemical examination of the pyrocatechol influence on Bray-Liebhafsky reaction after the oscillatory period (precisely after six regular oscillations) and the comparison of obtained results with those found under seme experimental conditions with pyrocatechol addition in the oscillatory mode/regime.

Experimental section

Bray-Liebhafsky experiments were carried out in a closed well-stirred (with stirring rate, σ = 900 rpm) reactor and thermostated at T = (60.0 ± 0.2) ^{o}C. The reaction volume was 55 ml, while the initial concentrations of reactants were: $[KIO_3]_0 = 7.35 \times 10^{-2}$ M, $[H_2SO_4]_0 = 4.79 \times 10^{-2}$ M, $[H_2O_2]_0 = 7 \times 10^{-3}$ M. All stock reactants solutions were pro analysis grade and prepared in deionized water. The moment when H_2O_2 was added to the vessel was taken as the beginning of the reaction. Different concentrations of the pyrocatechol were added (100 μl aliquot) into the reaction after the oscillatory regime, meaning after six regular BL oscillations (see Figure 2.). The electrochemical measurements were done in potentiometric mode. The time evolution of the BL reaction was followed by an iodide ion-selective electrode as a working electrode, and a double junction Ag/AgCl electrode as a reference electrode.

Results and Discussion

The recorded iodide ion-selective electrode-potential vs. time of the BL reaction without pyrocatechol addition is shown in Figure 2. From the presented oscillogram, it can be seen that

without pyrocatechol and under the above-mentioned conditions, the duration of the BL reaction is τ_{end} = 245 min. For that time system initially passes through the induction period, τ_{ind} = 55 min, after which six regular oscillations take place. It should be stressed that under the investigated experimental conditions the BL system exhibits only six oscillations, after which leaves oscillatory mode (τ_{end}).

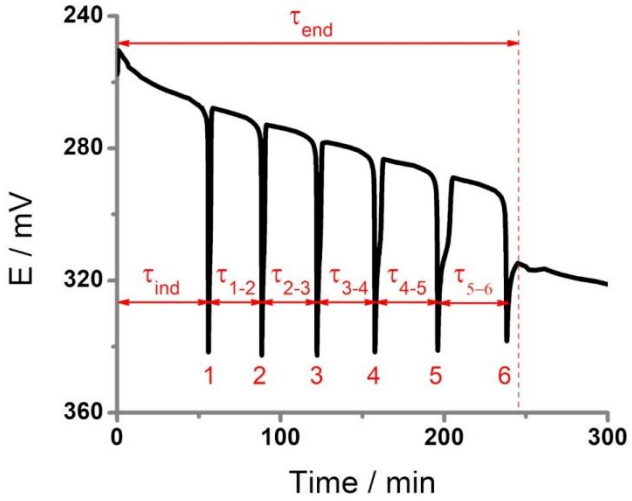

Figure 2. *Potential I⁻ ISE time series (oscillogram) of the Bray-Liebhafsky reaction obtained under batch reactor under following conditions* $[KIO_3]_0 = 7.35 \times 10^{-2}$ *M,* $[H_2SO_4]_0 = 4.79 \times 10^{-2}$ *M,* $[H_2O_2]_0 = 7 \times 10^{-3}$ *M, T = (60.0 ± 0.2 °C) and σ = 900 rpm, with marked oscillogram properties such as: induction period,* τ_{ind}*, periods between oscilations,* τ_{1-2}*,* τ_{2-3}*,* τ_{3-4}*,* τ_{4-5}*,* τ_{5-6}*, number of oscillations and duration of the oscillogram,* τ_{end}*.*

Herein, the influence of the pyrocatechol, in the range of its concentrations from 2.7×10^{-6} M to 1.2×10^{-4} M, on Bray-Liebhafsky reaction dynamics after the oscillatory period or accurately after six regular oscillations was investigated (Figure 3). Therefore, the pyrocatechol is added immediately after the sixth oscillation was completed in τ_{end}. As can be seen from Figure 3, pyrocatechol addition provokes the appearance of one more BL oscillation after the second induction period (denoted with τ^*). The influence of different pyrocatechol concentrations on the time between sixth and seventh oscillations is shown in Figure 4. It is clearly demonstrated that for investigated BL system, in a range of pyrocatechol concentration from 2.7×10^{-6} M to 1.2×10^{-4} M, the period between sixth and seventh oscillation shows linearity depending on pyrocatechol concentration, with the regression equation:

$$\tau^* = 2.3 \times 10^6 \times C_{Pyrocatechol} + 52.4,$$

(C is the concentration of pyrocatechol in BL system in M). The regression equation obtained for examined BL conditions, can be a useful tool for analytical purposes and accordingly, potential determination of unknown pyrocatechol concentration.

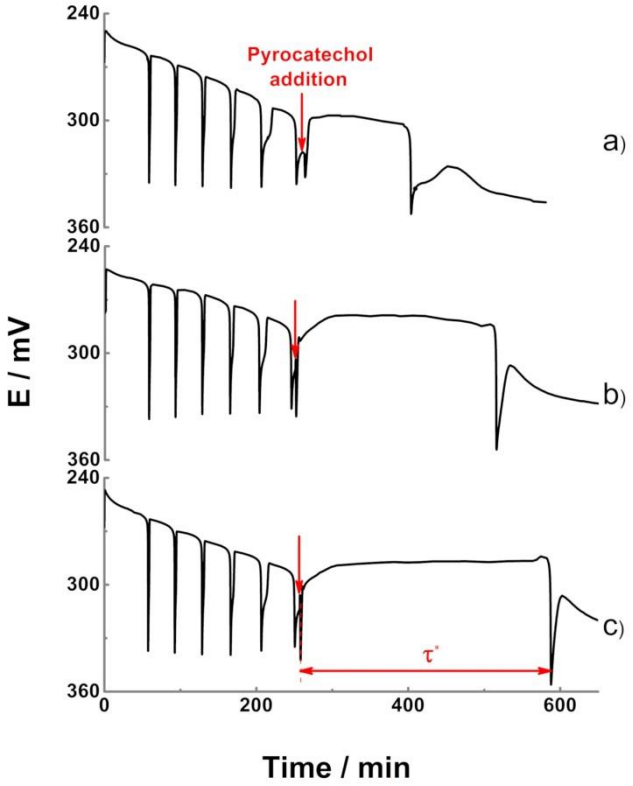

Figure 3. *Oscillograms of the BL reaction with different concentrations of pyrocatechol, added after sixth oscillation: 3.0 × 10^{-5} M (a), 9.0 × 10^{-5} M (b) and 1.2 × 10^{-4} M (c)*

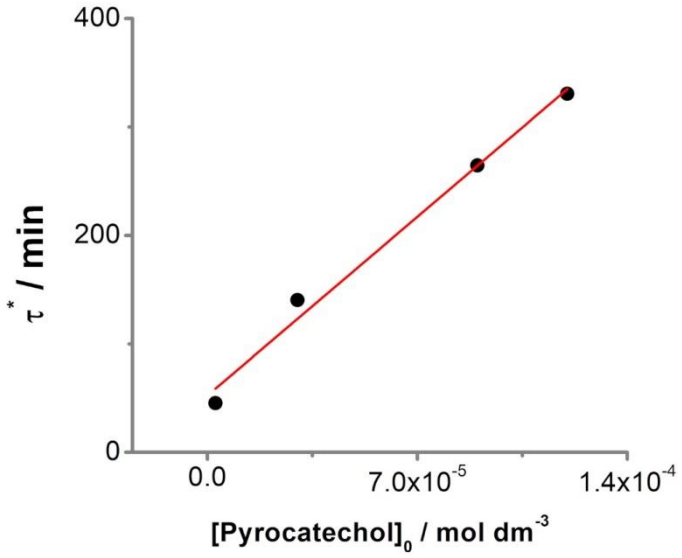

Figure 4. *The period between sixth and seventh oscillations dependence on pyrocatechol concentrations*

In our previous experiments, where the pyrocatechol was added in the oscillatory regime (after the second oscillation), the quenching of oscillatory dynamics has occurred. The new oscillation has appeared after so-called inhibitory period. Herein pyrocatechol is added after the oscillatory regime (precisely in the transient state) and the same behavior is obtained. Meaning the BL system has the second induction period after which one oscillation appears. In both cases, the linear dependence (with insignificantly different slope) of the second induction period (or inhibitory period when

pyrocatechol was added in oscillatory mode) *vs.* pyrocatechol concentration is obtained. Obtained results suggest that both BL modes (oscillatory and transient) could be useful for the experimental determination of pyrocatechol concentration.

Conclusions

This paper was investigated the pyrocatechol influence on the Bray-Liebhafsky reaction after the oscillatory period, precisely after six regular oscillations occurred. Afterward pyrocatechol addition, the BL system exhibits the second induction period after which one oscillation appears. For investigated BL system, in a range of pyrocatechol concentrations from 2.7×10^{-6} M to 1.2×10^{-4} M, the period between sixth and seventh oscillations shows linear dependence with added pyrocatechol concentration. The obtained regression equation can be a useful tool for analytical purposes and accordingly, potential determination of unknown pyrocatechol concentration. Obtained results suggest that both BL reaction modes: oscillatory (previously investigated) and transient (investigated in this paper) could be suitable for the experimental determination of pyrocatechol concentration.

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