Dynamic behavior of the Bray-Liebhafsky oscillatory reaction controlled by sulfuric acid and temperature

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INTRODUCTION

The investigation of chemical systems which possess non-linear properties such as self-organization and temporal dynamic structures has become one of the most active areas in chemical dynamics. Within the past several decade it has become apparent that the obtained results are of general relevance for other complex dynamics systems in various fields (life science, physics, mathematics, economy, and others) [1–3]. The Bray–Liebhafsky (BL) [4, 5] oscillatory reaction (the reaction where hydrogen peroxide decomposes into water and oxygen in the presence of both iodate and hydrogen ions) is a good example of the mentioned system; various dynamic states have been found in experiments and numerical studies of this nonlinear system [3, 6–27]. In this reaction system carried out in a continuously fed well stirred tank reactor (CSTR), changing control parameters such as the specific flow rate, temperature and inflow concentrations of the feed species [1, 2] may lead to the appearance of non-equilibrium stationary states, simple single-peak periodic oscillations, complex and chaotic dynamics. Transitions between these dynamic states are caused by various bifurcations [1, 2]. In investigation of chemical dynamical systems, bifurcations leading from simple steady states to periodic orbits, and vice versa, at a critical parameter value, are especially important. Those bifurcations are theoretically classified into four types [28], and can be studied and classified in dynamic systems by experimental means as well [29, 30].

The dynamics of BL reaction have been studied comprehensively in batch reactors [4, 5, 17–27], whereas there are only few studies in CSTR [6–10]. In the latter, the stable non-equilibrium stationary states, simple periodic oscillations, complex oscillations, bursts and deterministic chaos are discovered. These examinations have numerous intentions, from theoretical investigations and modeling [3, 11–16] of the considered system or related ones, to their application in analytical purposes with the aim to measure concentrations below current detection limits [31–34], or to depict kinetic characterizations of catalysts [8, 35–38]. Therefore, the dynamic states under various combinations of control parameters must be examined which is also the case in this paper.

Recently, we have studied [9] dynamic states of the BL oscillatory reaction varying the inflow concentrations of the sulfuric acid as a bifurcation parameter. According to our experiments there were intervals in the parameter space within which stable stationary states, simple periodic oscillations and complex aperiodic ones could be observed. We found that the transitions from the oscillatory to the nonoscillatory states went back and forth via SNIPER bifurcation, as well as some kind of the Andronov–Hopf bifurcation is presented. In addition, it was found that an increase of temperature, in different series of experiments resulted in the shift of bifurcation point towards higher values of sulfuric acid concentration.

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Abstract—The non-periodic, periodic and chaotic regimes in the Bray—Liebhafsky (BL) oscillatory reaction observed in a continuously fed well stirred tank reactor (CSTR) under isothermal conditions at various inflow concentrations of the sulfuric acid were experimentally studied. In each series (at any fixed temperature), termination of oscillatory behavior via saddle loop infinite period bifurcation (SNIPER) as well as some kind of the Andronov—Hopf bifurcation is presented. In addition, it was found that an increase of temperature, in different series of experiments resulted in the shift of bifurcation point towards higher values of sulfuric acid concentration.

Keywords: Bray—Liebhafsky, oscillatory reaction, control by sulfuric acid and temperature, Andronov—Hopf bifurcation.

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tion points, the dynamic behavior of the BL oscillatory reaction by varying inflow concentration of the sulfuric acid. Here, we have found precise conditions where transition from a stationary state to periodic oscillations, and vice versa, undergoes through both SNIPER and Andronov–Hopf bifurcation. Dynamic behaviors, as a transition from simple periodic oscillation to chaos have been also discovered. In addition, we want to show that an increase of temperature, in different series of experiments resulted in the shift of the observed bifurcation point towards higher values of sulfuric acid concentration.

**EXPERIMENTAL**

Only analytical grade reagents without further purification were used for preparing the solutions. Potassium iodate, sulfuric acid and hydrogen peroxide were obtained from Merck (Darmstadt, Germany). For the solutions of KIO₃, H₂SO₄ and H₂O₂, deionized water (ρ = 18 MΩ cm, Milli-Q, Millipore, Bedford, MA, USA) was used.

The experiments were conducted in a continuously fed well stirred tank reactor (CSTR). A schematic diagram of the instrumental setup is shown in [30]. In all experiments, the feed substances, aqueous solutions of H₂SO₄, KIO₃ and H₂O₂, were kept in reservoirs at room temperature and were introduced into reaction vessel separately without being previously thermostated.

The experiments were performed in a 50 ml glass reaction vessel (Metrohm model 876–20) shielded from light and surrounded by thermostating jacket. The volume of the reaction mixture was kept constant at V = 22.2 ± 0.2 ml by removing the surplus volume of the reaction mixture through the U-shaped glass tube, ending at the free surface over the reaction mixture. The solution was stirred magnetically (magnetic stirrer, Ingenieurbüro, M. Zipperer GmbH, Cat-ECM5, Staufen, Denmark) with a Teflon coated stir bar (polygon shaped 2 × 0.8 cm²).

The flows of the reactants through the reaction vessel were driven by peristaltic pumps (ISMATEC, Glattbrugg, Switzerland). Tygon tubes (Ismatec, Glattbrugg–Zürich, Switzerland) were used to transport the aqueous solutions of potassium iodate, sulfuric acid and hydrogen peroxide. These tubes were connected to teflon tubes (Varian, Darmstadt, Germany), and the reagents were introduced to the reaction vessel through them.

The temperature of the reaction mixture was controlled within ±0.1 K using a water bath (Julabo, series ED, Seelbach, Germany).

Temporal evolution of the system was recorded by means of a Pt electrode (Model 6.0301.100, Metrohm, Herisau, Switzerland) and double junction Ag/AgCl electrode (Model 6.0726.100, Metrohm, Herisau, Switzerland) as a reference. In the reference Ag/AgCl electrode, the inner electrolyte was a 3 mol l⁻¹ KCl and the outer electrolyte was a saturated solution of K₂SO₄.

For the investigated operation points, the BL reaction was run at elevated temperatures. Working at those temperatures causes evaporation of the electrolytes from the reference electrode. This causes a change of the measured potential value. Therefore, fresh electrolytes were added every morning in both the inner and the outer electrolytes compartment.

We investigated dynamic behavior of the BL reaction in the CSTR. These examinations were carried out in independent series of experiments (A, B, C, D and E) performed at different temperatures (T = 55.0, 58.0, 61.0, 64.0 and 67.0°C). In each series (at any fixed temperature), the dynamic behavior of the BL reaction was examined when the inflow concentration of sulfuric acid (control parameter) varied from 4.77 × 10⁻² to 9.78 × 10⁻² mol l⁻¹. In all experiments, [KIO₃]₀ = 5.90 × 10⁻² mol l⁻¹ [H₂O₂]₀ = 1.50 × 10⁻¹ mol l⁻¹ and the specific flow rate, j₀ = 2.95 × 10⁻² min⁻¹.

In the experimental procedure A, thermostated (water bath set at T = 55.0 ± 0.1°C) and protected from light, reaction vessel was filled with three separate inflows of the reactants, 5.90 × 10⁻² mol l⁻¹ KIO₃, 6.47 × 10⁻² mol l⁻¹ H₂SO₄ and 1.50 × 10⁻¹ mol l⁻¹ H₂O₂, at a maximum flow rate of 12 ml min⁻¹. Under these conditions, over 3.5 min, a nearly twice the volume of the reaction mixture was charged. Then, the inflows were stopped, the stirrer was turned on 900 rpm, and the excess reaction mixture was sucked out through a U-shaped glass tube to achieve an actual reaction mixture volume of 22.2 ± 0.2 ml. Hence, the reaction commenced under the bath conditions. After two bath oscillations (20 min) the inflows were turned on at the required specific flow rate (j₀) 2.95 × 10⁻² min⁻¹ and the inflow concentration of sulfuric acid was varied inside the interval, 4.77 × 10⁻² mol l⁻¹ ≤ [H₂SO₄] ≤ 9.78 × 10⁻² mol l⁻¹. Under the investigated conditions, it is sufficient to wait for three residence times (tᵣ = 1/j₀ ≈ 33.9 min) in order to obtain any stable dynamic structures for the examined inflow concentration of sulfuric acid.

The experimental procedures B, C, D and E are identical to the procedure A, except that the experiments were carried out at temperatures 58.0°C (procedure B), 61.0°C (procedure C), 64.0°C (procedure D) and 67.0°C (procedure E).

**RESULTS AND DISCUSSION**

Under conditions that are given in Experimental, different dynamic states are observed when inflow concentration of sulfuric acid varied from [H₂SO₄] = 4.77 × 10⁻² to 9.78 × 10⁻² mol l⁻¹. Characteristic examples of BL oscillograms obtained at temperature 61.0°C are illustrated in (Fig. 1, I–VII). The dynamic behavior of the BL reaction under CSTR conditions in
a function of the concentration of sulfuric acid as the control parameter (Fig. 1) i.e. bifurcation analysis, is presented by the related bifurcation diagram (Fig. 2). Moreover, the characterization of the bifurcation points in parameter phase spaces is performed.

Analyzing results obtained in (Figs. 1 and 2) at $T = 61.0^\circ$C, $[\text{KIO}_3]_0 = 5.90 \times 10^{-2}$ mol l$^{-1}$, $[\text{H}_2\text{O}_2]_0 = 1.50 \times 10^{-1}$ mol l$^{-1}$, $j_0 = 2.95 \times 10^{-2}$ min$^{-1}$, and concentration of sulfuric acid in the range from $4.77 \times 10^{-2}$ to $9.78 \times 10^{-2}$ mol l$^{-1}$ (experimental procedure C), distinct stable nonequilibrium stationary states characterized by approximately same potential values are found (for the respective intervals of concentration of sulfuric acid: $4.77 \times 10^{-2}$ mol l$^{-1}$ $\leq [\text{H}_2\text{SO}_4] < 5.50 \times 10^{-2}$ mol l$^{-1}$ (Fig. 2, zone I) and $8.06 \times 10^{-2}$ mol l$^{-1} \leq [\text{H}_2\text{SO}_4] < 9.78 \times 10^{-2}$ mol l$^{-1}$ (Fig. 2, zone IV) separated by an oscillatory evolution (for concentration of sulfuric acid in the range $5.60 \times 10^{-2}$ mol l$^{-1} \leq [\text{H}_2\text{SO}_4] < 7.69 \times 10^{-2}$ mol l$^{-1}$ (Fig. 2, zone II). However, for concentration of sulfuric acid in the range $7.82 \times 10^{-2}$ mol l$^{-1} \leq [\text{H}_2\text{SO}_4] < 7.99 \times 10^{-2}$ mol l$^{-1}$ (Fig. 2, zone III) a region of aperiodic oscillations is entered. At another operating points (experimental procedures A, B, D and the ranges of concentrations of sulfuric acid for which stable stationary states (zone I and IV) and regular oscillations (zone II) are obtained, and all are summarized in the table.

The lower bifurcation point (BP1) denoting the transition between stable and nonstable nonequilibrium stationary state is in the region $5.50 \times 10^{-2}$ mol l$^{-1} < [\text{H}_2\text{SO}_4] < 5.60 \times 10^{-2}$ mol l$^{-1}$, while the higher one (BP2) denoting the transition between nonstable and stable nonequilibrium stationary state obtained for higher values of sulfuric acid concentrations, is in the region $7.99 \times 10^{-2} < [\text{H}_2\text{SO}_4] < 8.06 \times 10^{-2}$ mol l$^{-1}$.

In this case, transition from the stable nonequilibrium stationary state (zone I, Fig. 2), into oscillatory (zone II, Fig. 2) goes through a saddle node infinite period (SNIPER) bifurcation that is based on the following certainties. When the bifurcation point BP1 is approached from the oscillatory side, the amplitudes of the oscillations remain constant, within experimental error, while the period of simple periodic oscillation increases exponentially. The bifurcation occurs for the inflow concentration of sulfuric acid having the value between $5.50 \times 10^{-2}$ and $5.60 \times 10^{-2}$ mol l$^{-1}$, the very same value as the one obtained with the increased sulfuric acid concentration; i.e., hysteresis was not observed. The bifurcation point is $[\text{H}_2\text{SO}_4]_{\text{BP1}} = 0.0532$ mol l$^{-1}$ and this value corresponds to the mean value of the concentration of sulfuric acid obtained from the two adjacent experiments which are lying on both sides of bifurcation point. In addition, in this case the period of oscillations in vicinity of BP1 rises to infinity, inversely proportional to the square root of the bifurcation parameter displacement, $\Delta = [\text{H}_2\text{SO}_4] - [\text{H}_2\text{SO}_4]_{\text{BP1}}$, i.e. $\tau \sim 1/\Delta^{1/2}$ [39]. A plot of period of oscillations versus $1/\Delta^{1/2}$ is a straight line, as shown in Fig. 3. By these quantitative observations, it can be
The concentrations of sulfuric acid (bifurcation parameter) for which stable stationary states (zone I and IV), regular oscillations (zone II) and complex oscillation (zone III) are obtained as well as the values of bifurcation points (BP1 and BP2) determined at different temperatures.

<table>
<thead>
<tr>
<th>( T, ^\circ C )</th>
<th>([H_2SO_4], \text{mol} \text{l}^{-1})</th>
<th>Critical values of bifurcation parameter (mol \text{l}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zone I</td>
<td>Zone II</td>
<td>Zone III</td>
</tr>
<tr>
<td>55.0</td>
<td>0.0477–0.0526</td>
<td>0.0538–0.0690</td>
</tr>
<tr>
<td>58.0</td>
<td>0.0477–0.0538</td>
<td>0.0550–0.0732</td>
</tr>
<tr>
<td>61.0</td>
<td>0.0477–0.0550</td>
<td>0.0560–0.0769</td>
</tr>
<tr>
<td>64.0</td>
<td>0.0477–0.0550</td>
<td>0.0560–0.0819</td>
</tr>
<tr>
<td>67.0</td>
<td>0.0477–0.0598</td>
<td>0.0610–0.0892</td>
</tr>
</tbody>
</table>

Note: Zones I and IV are regions of stable stationary states, zone II is region of simple periodic oscillations, zone III is region of complex dynamic. Chaotic dynamic (marked by asterisk) is obtained only for one inflow concentration of sulfuric acid. The values correspond to the mean value of the concentration of sulfuric acid (for BP1) which are obtained from the two adjacent experiments lying on both sides of bifurcation point. Locations of points PB2 are determined from the intercept on the abscissa of the linear extrapolation of the plot \( A^2 = \bar{f}(H_2SO_4) \).

Concluded that the transitions from the stable steady states to periodic orbits, and vice versa, proceed via SNIPER bifurcation [9, 29, 30, 39–41]. At another operating points (experimental procedures A, B, D and E), the same type of bifurcation is obtained. Those locations are contained in table. Thus, an increase of temperature, in different series of experiments resulted in slight a shift of the observed bifurcation point towards high values of sulfuric acid.

Transition from the oscillatory state (zone II, Fig. 2) to the stable nonequilibrium stationary state (zone IV, Fig. 2) goes through an aperiodic dynamic (Fig. 1, III–VI at 61.0°C and zone III, Fig. 2). Particularly, between \( 7.82 \times 10^{-2} \) and \( 7.99 \times 10^{-2} \text{ mol} \text{l}^{-1} \) (Fig. 1, III–VI), chaotic dynamics with different complexity are revealed. First, trains of burst-like large-amplitude oscillations emerge chaotically from an irregular procession of small-amplitude oscillations; the numbers of large oscillations as well as intervals between their emerging are chaotic. When inflow concentration of sulfuric acid is increased further, procession of large oscillations are shortened and number of small oscillations increases. In such way, for concentration of sulfuric acid \( 7.99 \times 10^{-2} \text{ mol} \text{l}^{-1} \) (Fig. 1, VI) only sequences of small-amplitude oscillations are obtained. Those periodic–chaotic sequences in system dynamics that are displayed always for the same value of bifurcation parameter may indicate the intermittent route to chaos [42].

This aperiodic dynamics, shown in (Fig. 1, III–VI) are terminated for \( [H_2SO_4] = 8.06 \times 10^{-2} \text{ mol} \text{l}^{-1} \) where a stable stationary state branch is reached (zone IV, Fig. 2). Comparing these results with the ones obtained when the inflow concentration of sulfuric acid decreased, the hysteresis is not observed. Last dynamic states with regular sustained oscillations that arise before the bifurcation point BP2 are analyzed by linear extrapolation of a plot of the square of the amplitude of regular periodic oscillations (Fig. 4). The critical value of the sulfuric acid concentration is \( [H_2SO_4]_{BP2} = 8.00 \times 10^{-2} \text{ mol} \text{l}^{-1} \). In addition, the period of oscillations in vicinity of this point \( [H_2SO_4]_{BP2} \) depends linearly on the bifurcation parameter displacement, \( \Delta = |[H_2SO_4] – [H_2SO_4]_{BP2}| \). Thus, we assume that the underlying dynamic structure consists of a stationary state loosing stability through probably Andronov–Hopf bifurcation [2], but the obtained intersection cannot be ascribed easily to this bifurcation point since two kinds of oscillations emerge from it [8–10]. Namely, between large amplitudes...
tude relaxations oscillations, observed close to the bifurcation point and stable nonequilibrium stationary state, relatively narrow chaotic window occurs.

At another operating points (A, B, D and E), as a rule, transition from the oscillatory state to the stable nonequilibrium stationary state goes through an aperiodic dynamic. Under those conditions, the concentrations of sulfuric acid for which aperiodic dynamics is obtained, are presented in table. Note that starting from lower acidity and increasing the inflow concentration of sulfuric acid, chaos is initiated from the large amplitude relaxation oscillations. On the other hand, as Vujković et al. pointed out [15], forms of chaos that were observed in the same concentration range between \(7.82 \times 10^{-2}\) and \(7.99 \times 10^{-2}\) mol l\(^{-1}\) at \(T = 61.0^\circ\text{C}\), in both directions, are different depending on the direction of sulfuric acid concentration change (Fig. 5). Moreover, they correlated experimentally the obtained time series with theoretically obtained difference between two chaotic dynamic states. However, on the basis of the obtained unusual chaotic series, it is impossible to determine the "route to chaos." Furthermore, we know from model simulations [12–15] that some of existing chaotic states occur within such a small domain of the control parameter values causing that experimental quantification of them is impossible, because stochastic fluctuations in the control bifurcation parameter drive dynamics among neighboring periodic states and chaotic regime. Thus, experimental obtained data should be analyzed using the tools of dynamic system theory [41–44] which is out of scope of this work.

However, as we described previously, the last dynamic states with regular sustained oscillations before bifurcation point are analyzed by linear extrapolation of a plot of square of the amplitude of the oscillations. The critical values of bifurcation parameter \([\text{H}_2\text{SO}_4]_{\text{BP}2}\) are summarized in table. Thus, in different series of the experiment that are obtained at different temperatures the type of bifurcation is not changed, but the temperature variation changes the position of bifurcation point. Similarly to temperature dependence of BP1, an increase of temperature, in different series of experiments resulted in a shift of the observed bifurcation points towards high values of sulfuric acid (table).

Recently [9] we studied dynamic states of the BL reaction when sulfuric acid is the control parameter under the following conditions: \(T = 56.0^\circ\text{C}\), \([\text{KIO}_3]_0 = 5.90 \times 10^{-2}\) mol l\(^{-1}\), \([\text{H}_2\text{O}_2]_0 = 1.50 \times 10^{-1}\) mol l\(^{-1}\), \(j_0 = 2.95 \times 10^{-2}\) min\(^{-1}\) and the inflow concentration of sulfuric acid varied from \([\text{H}_2\text{SO}_4] = 4.22 \times 10^{-2}\) to 9.00 \(\times 10^{-2}\) mol l\(^{-1}\). For these conditions, the same types of bifurcations were found as in the present work; transitions from the stationary state into oscillatory and vice versa go through both, the SNIPER bifurcation and some kind of the Andronov–Hopf bifurcation. Moreover, very similar to this work, a chaotic behavior is emerging in the vicinity of the Andronov–Hopf bifurcation. The same behavior was found by investigation of dynamic of BL reaction when temperature was bifurcation parameter [8]. In addition, in all cases a linear response of the squares of amplitudes with respect to control parameters where found, but these intersections cannot be simple Andronov–Hopf...
bifurcation points. So, in all cases, those bifurcation points are similar and these are rather complex since two kinds of oscillations emerge from them.

CONCLUSIONS

Dynamic behavior exhibited by BL reaction under different experimental conditions in the CSTR is performed. When the inflow concentration of sulfuric acid was varied, different types of dynamic regions including stable non-equilibrium stationary states, simple periodic oscillations and chaotic mixed-mode oscillation were noticed. The experimental evidence for the onset and termination of oscillatory behavior via the saddle node infinite period (SNIPER) bifurcation as well as some kind of Andronov—Hopf bifurcation are presented. Finally, the temperature variation in different series of experiments does not change the type of bifurcation point, but rather its value.

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REFERENCES


