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Effects of the electrolytes in a closed unstirred Belousov–Zhabotinsky medium

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Abstract

Complex periodic and aperiodic behaviors are reported in an unstirred Belousov–Zhabotinsky reaction at different concentrations of added electrolytes. A route to chaos following a Ruelle–Takens–Newhouse (RTN) scenario is identified. A *3-fold torus* was also found in phase space. In this paper, we prove that the concentration of inert added electrolytes is a bifurcation parameter for the sequence period-1 → period-2 → period-3 → chaos.

Keywords: Belousov–Zhabotinsky; Nonlinear dynamics; RTN scenario; Transient chaos; Electrolytes; Sulphate ions

1. Introduction

The Belousov–Zhabotinsky (BZ) reaction is the most famous oscillatory chemical reaction in a homogeneous liquid phase for studying temporal, spatial and spatiotemporal nonlinear dynamics in nonequilibrium systems [1–3]. Significant research has been undertaken to understand chemical chaos that have been usually observed in a continuously flow stirred tank reactor (CSTR) [1,3,4]. It has been also reported that transient chaotic oscillations are observed in the BZ oscillating chemical reaction in a stirred batch reactor experimentally and numerically [5–8].

Recently, we have observed aperiodic oscillations during the chemical evolution of a closed unstirred cerium catalyzed BZ system [9]. These aperiodic oscillations are an example of transient chaos because they are sensitive to the initial conditions, the major distinctive features of chaos [9,10]. The chaotic regime is bounded by two periodic zones. The onset of chaos spontaneously starts by a Ruelle–Takens–Newhouse (RTN) scenario [11,12] as soon as convection motion couples to diffusion and local kinetics. The chaotic motion continues for about 2 h and ends by an inverse RTN scenario [13]. Differently from the first transition (RTN scenario), the last seems related to the consumptions of the reactants [12,13]. In previous papers, we studied the effect of different experimental conditions on the system dynamics. We showed that viscosity, temperature and reactor geometry are important control parameters for the transition to chaos [14–17]. They play an important role in the coupling of chemical kinetics, diffusion and convection allowing or preventing the onset of chaos. A common feature of these systems is that the transition to chaos always takes place through an RTN scenario.

In this paper, we will show that the added electrolyte concentration is another bifurcation parameter responsible for the transition chaos to periodicity of a closed unstirred BZ reaction.

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2. Experimental

All experiments were performed isothermally at ~20 °C in a batch reactor (spectrophotometer cuvette, $1 \times 1 \times 4\ cm^3$). The dynamics were monitored by the solution absorbance at 320 nm using quartz UV grade spectrophotometer cuvettes. A double beam spectrophotometer (Varian, series 634) was used. All chemicals were of analytical quality and were used without further purification. The following concentrations of reactants stock solutions were used: $Ce(SO_4)_2$ 0.004 M, malonic acid 0.30 M, $KBrO_3$ 0.09 M; each stock solution was 1 M H_2SO_4. The oscillator was started by mixing equal quantities of reactants in a flask. Several experiments were performed by adding $Na_2SO_4 \cdot 10H_2O$, $MgSO_4$ or $Al_2(SO_4)_3$ to the solution at different concentrations. The solution was stirred for 10 min with a 1-cm length teflon-coated magnetic stirrer, at a constant high stirring rate; then electrolytes were added and the solution was stirred for another 2 min, the total volume was 12 ml.

The solution was then poured into the cuvette until the sample reached the top, and measurement of the signal began. The cross-sectional area of the spectrophotometer light beam was $30\ mm^2$. The volume spanned by the beam was $300\ mm^3$ (7.5% of the total volume) and was located 2 cm away from the liquid-air interface, 1 cm away from the bottom of the cuvette and about 0.4 cm away from the sides.

The spectrophotometer was connected to an IBM compatible PC for data acquisition by an analog to digital board converter with a 16-bit resolution. The absorbance was recorded with a $\tau_s = 1$ s sampling time. Time series points were recorded and stored in the computer for data analysis.

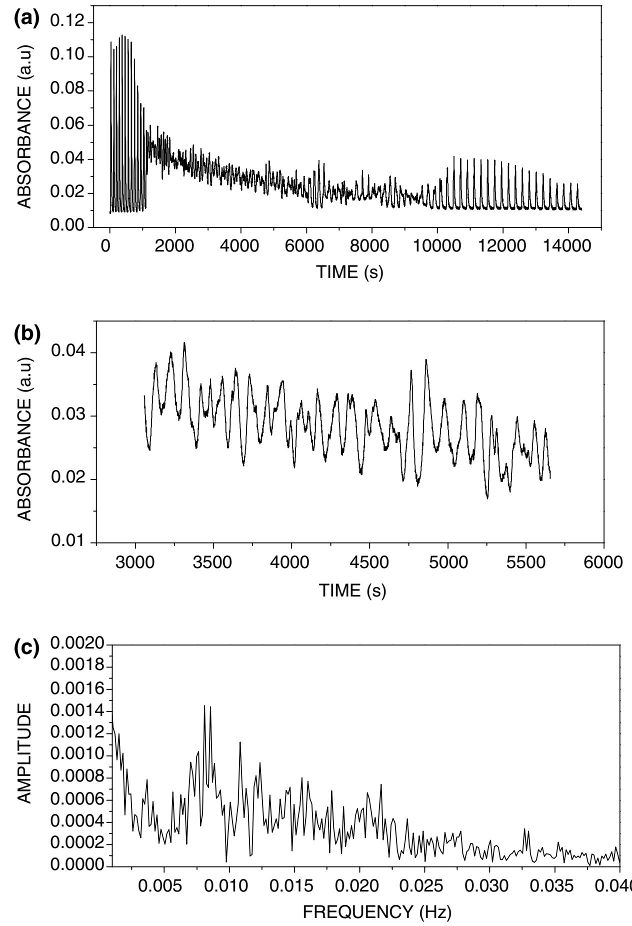

Fig. 1. (a) A typical spectrophotometric recording in absence of stirring. (b) Time series of the region 3058–5656. (c) Typical broad band spectrum of a chaotic regime in the Fourier transform of the region 3058–5656.

3. Results

In this section, we will illustrate in detail the results obtained adding Na_2SO_4 to the BZ solution; we obtained analogous results for the others electrolytes. Fig. 1(a) shows the typical spectrophotometric recording in absence of stirring. Two transitions: periodic → aperiodic → periodic can be observed. The Fourier transform of a significant interval of the aperiodic region (Fig. 1(b)), shows a broad band spectrum (Fig. 1(c)); it is a common feature of all aperiodic time series. Our previous experiments [9,12,13] show that these aperiodic oscillations of the BZ system are an example of chaotic transient. For this reason we can refer to this behavior by the following scheme: periodicity → chaos → periodicity.

Fig. 2(a) shows a typical spectrophotometric time series recording after 0.2707 g of Na_2SO_4 (0.070 M) was added to the BZ solution. This spectrum is not distinguishable from that obtained in absence of Na_2SO_4. Fig. 2(b) shows an aperiodic pattern like that obtained in absence of Na_2SO_4 (Fig. 1(b)). In fact the Fourier transform (Fig. 2(c)) of the signal shown on Fig. 2(b) (range 3058–5656 s) presents a typical broad band spectrum like that of Fig. 1(c). The Fourier transform is not able to distinguish between chaos or random motion as both give broad band spectra, nevertheless there is no reason to believe that Na_2SO_4 can induce a transition from chaos to random motion. Therefore the behavior that appears on Fig. 2(a) is a manifestation of chaos. This type of behavior does not change until the Na_2SO_4 concentration reaches a critical concentration of about 0.087 M.

When Na_2SO_4 concentration reaches 0.087 M the aperiodic pattern disappears and only the periodic behavior occurs as showed in (Fig. 3(a)). In fact the Fourier transform (Fig. 3(b)) of this region is nearly sinusoidal with only harmonics of the fundamental frequency ($f_1 \sim 0.00579$ Hz) above the noise level.