Role of the Reactor Geometry in the Onset of Transient Chaos in an Unstirred Belousov−Zhabotinsky System

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Received: October 15, 2002; In Final Form: February 24, 2003

The dynamics of the Ce(IV)-catalyzed Belousov−Zhabotinsky (BZ) system has been spectrophotometrically monitored at 20.0 °C in unstirred batch conditions by using cuvettes with different geometry. The cuvette path length has been varied from 1 to 0.02 cm. The experimental results have shown that when the cuvette path length is in the range 1−0.05 cm the BZ system exhibits a chaotic behavior while below the critical value of 0.05 cm the dynamics of the BZ system is periodic. These trends have been ascribed to the elimination of the convective effect below a critical threshold and unambiguously demonstrate that convection is a bifurcation parameter for the route to chaos.

Introduction

Oscillatory chemical reactions and related temporal and spatial phenomena have been observed in many homogeneous and heterogeneous systems.[1] The Belousov−Zhabotinsky (BZ) reaction is the most famous oscillatory chemical reaction in a homogeneous liquid phase that makes up a model for studying temporal, spatial, and spatiotemporal nonlinear dynamics in nonequilibrium systems.[1−3] Vigorous research has been undertaken to understand chemical chaos that has been usually observed in a continuous-flow stirred tank reactor (CSTR).[1,3,4] Moreover, transient chaotic oscillations are observed in the BZ oscillating chemical reaction in a stirred batch reactor experimentally and numerically.[5−10] An unstirred closed BZ system during the normal chemical evolution before reaching equilibrium spontaneously shows the following sequence of dynamic behavior: period-1 → quasiperiodicity → chaos → quasiperiodicity → period-1. Two transition scenarios, that is, at the onset of chaos and at its end, are observed. One appears as the mirror image of the other. These two transitions have been ascribed, respectively, to a direct and an inverse Ruelle−Takens−Newhouse (RTN) scenario.[11−14] The onset of chaos spontaneously starts as soon as convection motions couple to diffusions and kinetics. The convective motion is due to the hydrodynamic instability of the system, which may be caused by density difference between the reacted and unreacted fluid, thermal gradients, and an interplay of the two different effects. The different density, measured at the same temperature, between the reacted and unreacted fluid leads to an instability similar to the classical Rayleigh−Taylor instability, while, if there is a large enough temperature difference, the density gradients caused by the thermal gradients can result in a Rayleigh−Bernard-like instability.[15−17] As it is well-known, the hydrodynamic effect can be either practically eliminated by stirring the solution or significantly diminished by increasing medium viscosity.[18] Addition of micelle-forming surfactants, polymers, and other macromolecules as well to an aqueous solution allows one to achieve this purpose, and the extent of the increase depends[19] on the nature of the additive used. In fact, the contribution to the solution viscosity is greater for nonionic additives than for the anionic ones.

To ascertain the role played by the convection in the onset of chaos, we have previously[20−22] investigated the behavior of the unstirred Ce(IV)-catalyzed BZ system in the presence of nonionic additives, namely, poly(ethylene glycol) and hexa(ethylene glycol) monodecyl ether and hexa(ethylene glycol) monotetradecyl ether. In all cases, it has been found that when different amounts of the nonionic additives are added to the BZ system the chaotic dynamics interval disappears by a RTN scenario. This behavior has been attributed to the enhancement in the medium viscosity. Thus, the additives concentration, and as a consequence the medium viscosity, has been set as a bifurcation parameter for the chaos−periodicity transition in an unstirred batch reactor. Nevertheless, we have to take into account that the additives can influence the kinetics of the chemical reactions; thus, it seemed necessary to us to eliminate the convective motion of BZ reactive in a way that does not interfere with the kinetic of reaction. As many theoretical and experimental studies extensively demonstrate,[17,23−26] chemical waves travelling in tubes and channels containing excitable BZ-reaction mixture show a very intriguing nature because the ascending and descending waves have different speed. Because it is well established that ascending and descending waves are equal and constant with respect to changes in the tube diameter, it seems clear that the changes in wave speed are the result of convection driven by the density gradients associated with travelling chemical wave. Below a critical tube diameter, both ascending and descending waves travel at the same speed, which is independent of the tube diameter. Bearing in mind all of this information and with the aim at further establishing whether the disappearance of the chaotic behavior is due to the enhancement in the medium viscosity as a consequence of the

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10.1021/jp027213q CCC: $25.00

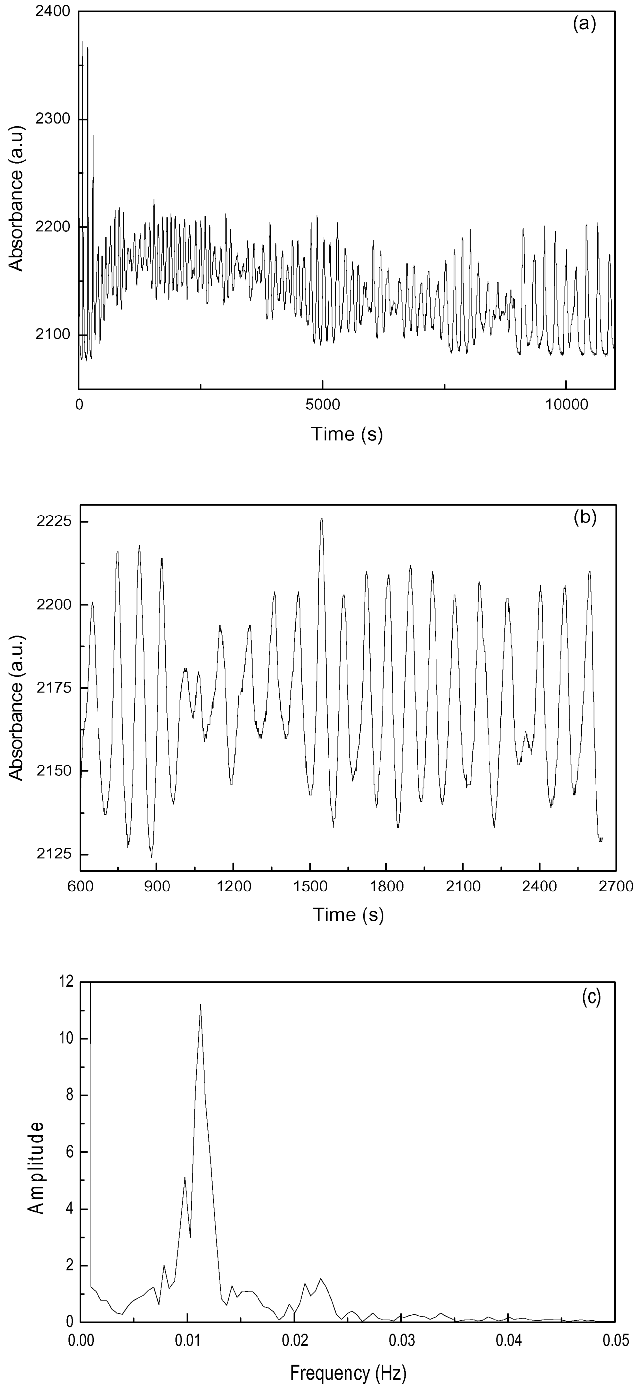

Figure 1. Spectrophotometric recording (a) of the Ce(IV) absorbance in the absence of stirring, (b) details of spectrum a in the range 600−2700 s, and (c) fast Fourier transform of spectrum b evidencing a broadband spectrum typical of the chaotic signal ($\lambda = 350$ nm, cuvette path length = 1 cm, $\tau_s = 1$ s, $t = 20$ °C).

elimination of the convective effect, we have performed a spectrophotometric study on the dynamic behavior of the BZ system in unstirred batch conditions by using cuvettes with different geometry. The cuvette path length has been varied from 1 to 0.02 cm.

Experimental Methods

Potassium bromate, $Ce(SO_4)_2 \cdot 4H_2O$, malonic acid, and sulfuric acid were of commercial analytical quality (Fluka) and used without further purification. Deionized water from reverse osmosis (Elga, model Option 3), having a resistivity higher than 1 MΩ cm, was used to prepare all solutions. Stock solutions of sulfuric acid were standardized by acid−base titration.

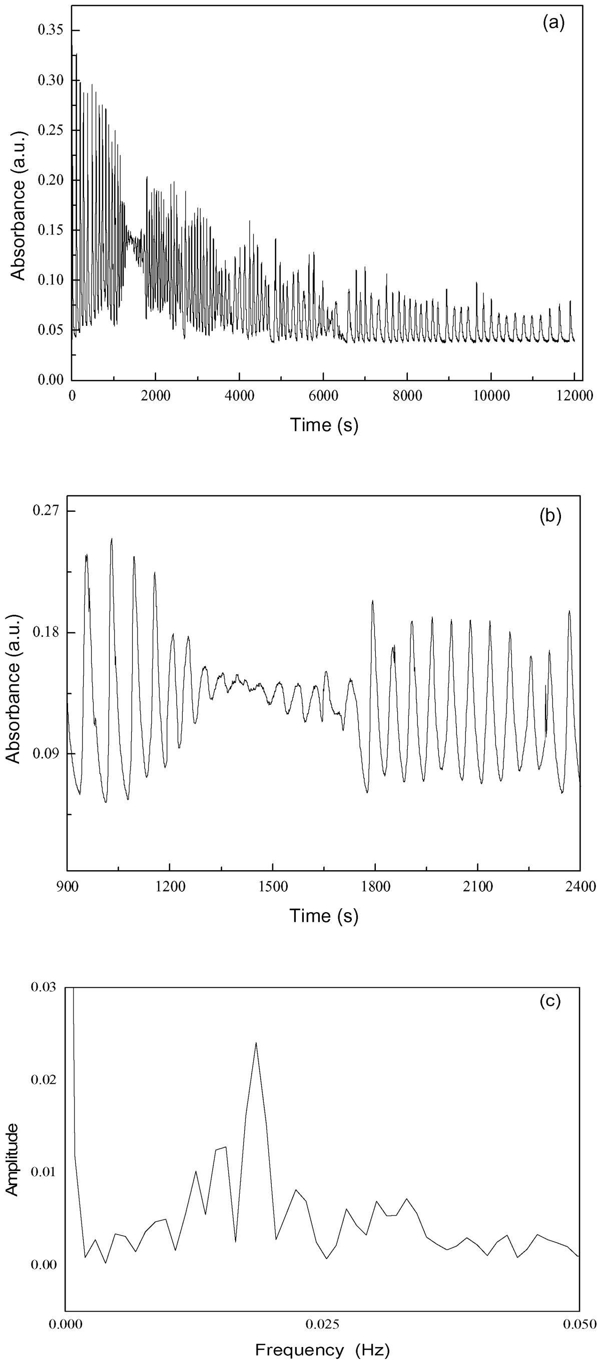

Figure 2. Spectrophotometric recording (a) of the Ce(IV) absorbance in the absence of stirring, (b) details of spectrum a in the range 900−2400 s, and (c) fast Fourier transform of spectrum b evidencing a broadband spectrum typical of the chaotic signal ($\lambda = 350$ nm, cuvette path length = 0.1 cm, $\tau_s = 1$ s, $t = 20$ °C).

The unstirred kinetics runs were performed in a batch reactor, and the dynamics of the system were monitored by following the Ce(IV) absorbance changes at 350 nm with a computer-controlled Beckman model DU-640 spectrophotometer, equipped with thermostated compartment for the cuvettes. Quartz UV grade spectrophotometer cuvettes have been used, and the cuvette path length has been varied from 1 to 0.02 cm. The oscillator was started by mixing equal volumes of reactant solutions in a flask. This solution was stirred for 10 min with a Teflon-coated magnetic stirrer of 1 cm length at a constant

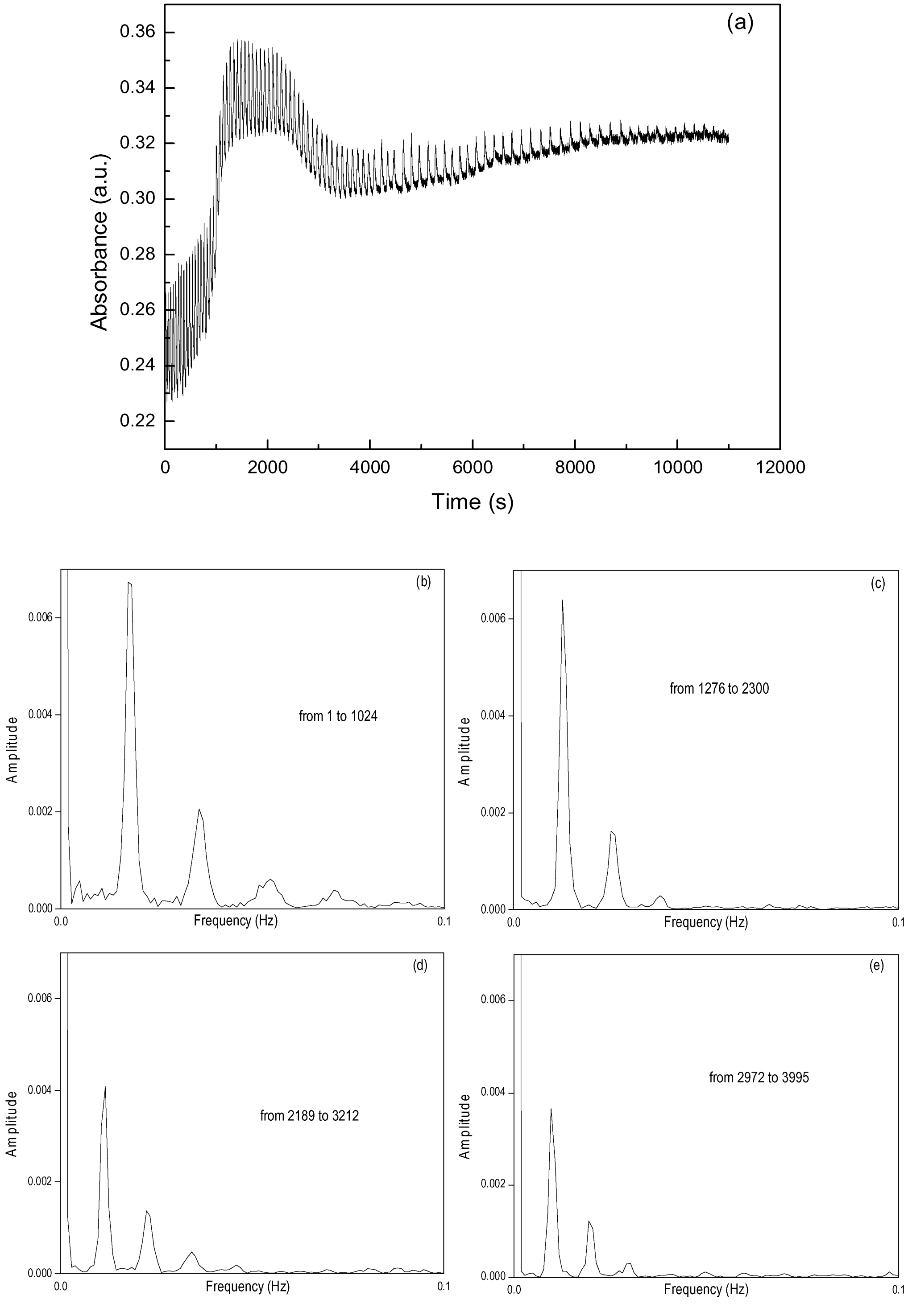

Figure 3. Spectrophotometric recording (a) of the Ce(IV) absorbance in the absence of stirring, and (b−e) fast Fourier transform of four consecutive intervals showing fundamental frequencies and few harmonics. These are typical patterns of periodic signals. The frequency decreases in time as reagents are consumed ($\lambda = 350$ nm, cuvette path length = 0.05 cm, $\tau_s = 1$ s, $t = 20$ °C).

high stirring rate. The solution was then poured into the cuvette, and measurement of the signal began. The absorbance was recorded with a sampling time (τ_s) of 1 s. Time series points were recorded and stored in the computer for data analysis. The spectral analysis was performed by fast Fourier transform (FFT), by using the computer program Origin 6.0 (Microcal Software, Inc)[27] on sequential 1024 point portions of a time series. To increase the spectral resolution, we applied the zero filling technique. The short time fragments (1024 points) were transformed into longer time series sequences (2048 points) by adding a constant value equal to the minimum of the signal amplitude at the end of the fragments. In this way, the spectral resolution $\Delta f = 1/(N\tau_s)$, where N is the number of points of the considered time fragment and τ_s is the sampling time, was doubled. Discontinuities at the window edges have been reduced by multiplying to the considered data a Hanning window function.[28] This operation suppressed side lobes, which would otherwise be produced in the power spectrum of the signal. The following concentrations of reactants were used: Ce(IV) 0.004 mol dm^{-3}, malonic acid 0.30 mol dm^{-3}, $KBrO_3$ 0.09 mol dm^{-3}. The temperature of all of the experiments was regulated to 20.0 ± 0.1 °C with a thermostat Heto model DT HetoTerm.

Results and Discussion

The spectrophotometric time series recorded by following the dynamic behavior of the unstirred BZ system in a cuvette with path length of 1 cm is reported in Figure 1a. As for the central part of temporal series (Figure 1b), the FFT, which result is shown in Figure 1c, confirms that chaotic behavior arises during the dynamic evolution of the reaction. A broadband spectrum typical of chaotic systems is obtained. The broadband spectrum does not discriminate between chaos and random motion. Nevertheless, this system[9,10] shows the dependence on the initial conditions, which is one major distinctive signature of chaos. Actually the chaotic regime observed in Figure 1b is bounded by two quasiperiodic zones. The existence of a torus can be detected at the onset of chaos and at its end, and a Ruelle−Takens−Newhouse scenario[12] occurs. The chaotic behavior has been attributed[12] to the interplay between chemical kinetics and diffusion−convection processes. Similar trends to that evidenced in Figure 1a have been obtained by performing the experiments in cuvettes having path lengths of 0.5, 0.2, and 0.1 cm. For the sake of simplicity, only the experimental results concerning the 0.1 cm cuvette are given in Figure 2a. The FFT of the temporal series proves that the dynamics of the BZ system is still chaotic (Figure 2c), even if perusal of Figure 2b clearly shows that the chaotic region becomes very short as the reactor path length is decreased. As for the oscillatory behavior of the BZ system in cuvettes having a path length of 0.05 and 0.02 cm, it has been found a very interesting behavior. A typical result is shown in Figure 3a. We can observe that during the acquisition one or more absorbance jumps localized in random positions on the temporal series occur. We have ascribed these jumps to the formation of bubbles of CO_2 in the reactor because for all experiments we carried out the absorbance jump in the time series appears in a different point. Moreover, the FFT analysis always shows that the dynamics is periodic. The spectrum of Figure 3a was divided into four intervals, and the results of the fast Fourier transform analysis are shown in Figure 3b−e. The FFT reveals the existence of the fundamental frequency and few harmonics. Nevertheless, the frequency of the oscillations decreases in time as reagents are consumed. As a matter of fact, our reactor is closed and the chemical reaction will reach thermodynamic equilibrium. From a dynamical point of view, in phase space this should be a slowly winding spiral. In a short period of time, the signal is almost stationary and the trajectory is approximately a limit cycle in phase space.

The observed effect of the reactor geometry on the behavior of the BZ system can be explained taking into account that, as it has been found by Pojman et al.,[23] the convection is observed only in tube having a radius of 0.089 cm while it disappears when the tube radius is 0.047 cm. These results imply that until we use a convective cell the BZ system shows a chaotic pattern, even though as the path length becomes smaller, the chaotic region becomes shorter. Below the critical threshold of 0.05 cm, when no convection is expected, the BZ system is forced to give a periodic behavior. This result is in agreement with theoretical and experimental observations.[15,23,25,26,29]

We can conclude that the decrease in the cuvette path length, that is, the convection is switched off, prevents the onset of chaos. This sets the reactor geometry as a bifurcation parameter of the unstirred BZ system, and as the parameter is changed, a chaotic attractor appears or disappears depending on whether the cuvette path length increases or decreases. This conclusion is supported by numerical results. Wu et al.[25,26] studied the onset of convection for the BZ system in a 2-D vertical slab; they found that below a critical slab width (0.37 mm) globally stable conventionless waves exist and have a constant speed (~8.95 mm/min). Furthermore, above this critical value, the chemical wave velocity increases giving rise to the onset of convection; the kinetic energy increases with the slab width. In our experiments, we noticed indirectly the effect of increasing kinetic energy. As we already pointed out, the chaotic regime lifetime is longer for longer path length of the cuvette; it is likely that it is harder for the system to dump down convective motion of higher kinetic energy and to go back to the periodic regime.

The results obtained in the present work together with those previously found[20,21] lead to the concluding suggestions and unambiguous demonstration that onset of chaos in the unstirred BZ system significantly depends on the convection. In fact, the way that we eliminate the convection does not matter, that is, either by adding increasing amounts of nonionic additives or by decreasing the cuvette path length; the BZ system undergoes a chaos to periodic transition when the interplay between chemical kinetics and diffusion−convection cannot take place.

Acknowledgment. This work was supported by MIUR (Italy).

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