New Types of Mixed-Mode Periodic Oscillations in the Belousov−Zhabotinsky Reaction in Continuously Stirred Tank Reactors

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Complex periodic oscillations with small amplitude oscillations close to the maximal value of a large amplitude oscillation followed by other small amplitude oscillations close to the minimal value of the next largest amplitude oscillation are found in the Belousov−Zhabotinsky (B−Z) reaction (bromate−malonic acid−ferroin) in CSTR. Oscillations showing identical patterns are obtained in a simple model proposed recently for a qualitative description of transient and asymptotic oscillations observed in the B−Z system.

I. Introduction

Various complex periodic as well as chaotic oscillations have been observed experimentally in continuously stirred tank reactors (CSTRs) in asymptotic regimes.[1−8] The periodic oscillations observed so far exhibit patterns of the type LS_n, where L denotes oscillations with large amplitude and S means oscillations with substantially smaller amplitudes as compared with L, and $n = 0, 1, 2, ...$ In these patterns S oscillations had their minima close to maximal values of L amplitudes or (but not and) they had their maxima close to minimal values of L. To our best knowledge, complex periodic oscillations in which one type of small amplitude oscillations have their minima at maximal value of L and, in the same pattern, other small amplitude oscillations with maxima close to minimal value of L have not yet been observed in chemical systems. In order to distinguish between these two small amplitude oscillations, we will use the notation LS_ns_m, where S_n is for n small amplitude oscillations close to the maximum of L and s_m is for m ones close to minimum of L. Such patterns have been found in some models of dynamical systems, namely in the Lorenz model,[9] and its modifications,[10] and also in models concerning periodic perturbations of the Duffing−van der Pool oscillator.[11]

We present experimental examples of complex periodic oscillations that have the patterns described above. We have found them in the B−Z reaction catalyzed by ferroin. Moreover, we show that qualitatively identical oscillations can be obtained in a simple model that was constructed recently in order to describe various patterns of transient and asymptotic complex periodic oscillations observed in the B−Z system.[12,13]

II. Experimental Results

Analytical grade chemicals $KBrO_3$, H_2SO_4, phenanthroline ("POCh" S.A. Gliwice), and malonic acid (Aldrich) were used without further purification. $FeSO_4 \cdot 7H_2O$ was synthesized by the authors. Ferroin solution was prepared according to the standard method. All solutions were prepared by using double-distilled water. Measurements were carried out in a continuously stirred tank reactor (CSTR) at a temperature of 21 °C, which was measured in the reaction mixture. CSTR had a Teflon cover, which allowed us to adjust the volume of the reaction mixture. In the experiments reported in this paper the volume of the reaction mixture was equal to 40 cm^3. The stirring rate was 900 rpm. A peristaltic type pp 1-05A (Zalimp) pump with three independent inlets was used to lead the reagents into the reactor. One inlet was used to pump the mixture of MA and H_2SO_4, and two others were used for ferroin and bromate solutions. The initial concentrations of the reactants in the reaction mixture were equal to $[KBrO_3] = 0.19$ M, $[MA] = 0.68$ M, $[H_2SO_4] = 0.32$ M, and $[Fe(phen)_3{}^{2+}] = 3.13 \times 10^{-3}$ M. The state of the system was followed by simultaneous measurements of potentials of platinum and bromide electrodes using a saturated calomel reference electrode connected with the reaction mixture by a salt bridge with 1 M KNO_3. Changes of the potentials in time were recorded by a MTA (Kutesz, type 1040/4) recorder and by a PC computer. The residence time τ was changed from about 1 h to about 6 min. The measurements were performed up to a dozen or so residence times in order to achieve asymptotic regimes.

We assumed that the system achieved the asymptotic regime when a sequence of the oscillations in the periodic pattern observed repeated at least dozen times. We have to notice that transient times to attain the asymptotic patterns varied in repeated experiments from several to a dozen residence times. During the transient regime the system exhibits sometimes irregular (rather stochastic than deterministic chaotic) oscillations.

Experiments on transient behaviors in this system but for long residence times have been reported recently.[13] Here we present the results for much shorter residence times and limit ourselves to asymptotic regimes. A new type of pattern has been observed at $\tau = 10$ min. After 8τ changes of the electrode potentials became almost periodic and the pattern LS_2s_{11} was observed in long time intervals (see Figure 1a,b)). In this figure we show only the small interval of the asymptotic regime. The Br^- electrode potential exhibits a large amplitude peak (L) followed by two small amplitude peaks (S) before the potential reaches its minimal value, and the next eleven well seen, much smaller amplitude peaks (s) appear on the ascending part of the potential

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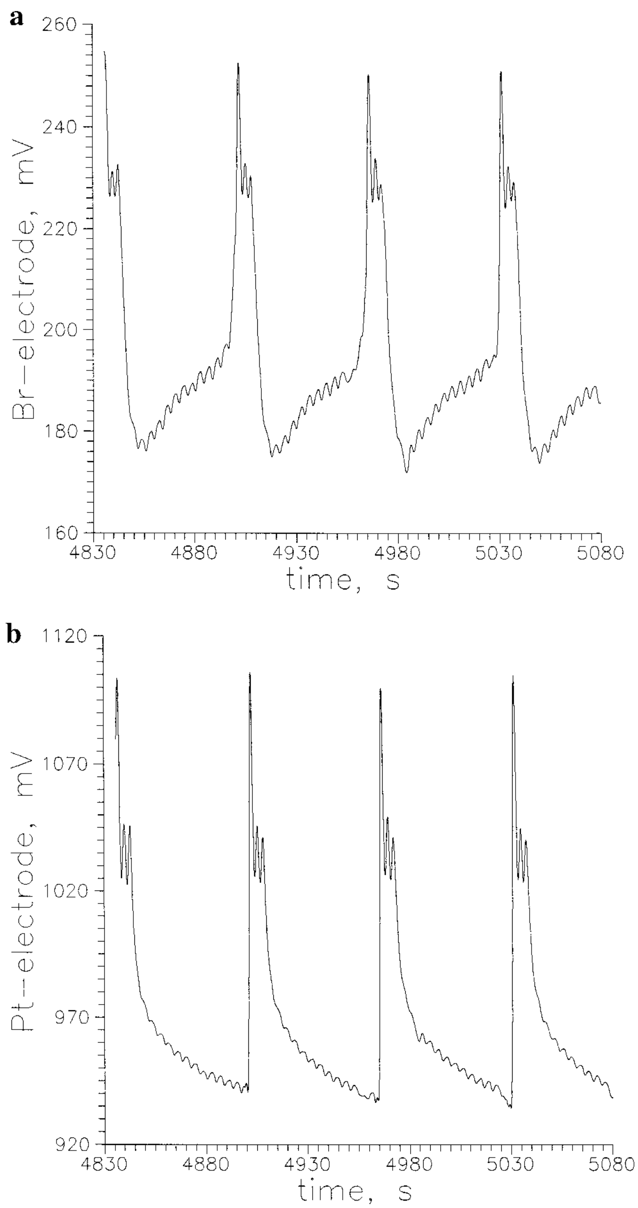

Figure 1. Time oscillations of potentials of Br (a, top) and Pt (b, bottom) electrodes for the CSTR experiment for residence time τ = 10 min. The asymptotic pattern LS_2s_{11} is shown.

before the subsequent large amplitude peak appears. The changes of the Pt electrode potential are almost synchronous with the Br^- electrode signals. However, much smaller amplitude peaks appear on the descending part of the potential before it reaches its maximum. Eleven well-distinguished small such peaks are seen in Figure 1. In the course of the experiment some of these peaks disappear but, instead, there appear changes of the sign (from positive to negative) of the second derivative of the potentials that are called "shoulders". The total number of peaks and shoulders remains equal to eleven.

Repeated experiments gave similar results. The pattern LS_2s_{11} has been observed in most of them, however, not all s peaks and shoulders were so clearly shaped as those shown in Figure 1. This can be explained by changes of τ in the course of the experiments as well as by variation of τ from one experiment to another. In all our experiments a maximal error of the residence time was about 10%.

If τ was sufficiently long (larger than 27 min), only large amplitude peaks L were observed in the asymptotic regime. For τ = 20 min the system exhibited a "mixture" of L and LS_1 and (irregular in their heights) s type small oscillations. For τ = 16 min only the LS_1 pattern was observed without any small oscillations of the type s, whereas for τ = 12.8 min we observed a mixture of LS_2 and LS_1 without s type small amplitude oscillations. The pattern shown in Figure 1 was observed for τ = 10 min. For τ = 7.8 min the system exhibits again the new pattern, namely LS_3s_{13}. Decreasing τ to 6 min, we observed the LS_4s_n pattern in which a dozen small amplitude oscillations of type s appeared. These oscillations were not distinctly shaped, and it was difficult to determine their number. Each τ experiment was repeated at least two times. The pattern shown in Figure 1 had been obtained in four out of five repeated experiments. In the "unsuccessful" case we probably observed a transient regime in which s type oscillations appeared but the reproduction of the pattern was unsatisfied, although we run the experiment longer than 20 residence times.

III. Model

Recently,[12−14] we have suggested a simple four-variable model that qualitatively describes regularities observed in transients as well as asymptotic mixed-mode oscillations in the BZ reaction

$$\dot{v} = a[u - (v - v_1)(v - v_2)(v - v_3) - a] = af(u, v) \quad (1)$$

$$\dot{u} = b - b_1 p - b_2 v - u = g(u, v) \quad (2)$$

$$\dot{p} = q(v - p) \quad (3)$$

$$\dot{q} = -\gamma(q - q_1) \quad (4)$$

For the asymptotic regime this model reduces to the three-variable model described by (1)−(3) with $q = q_1$. A detailed analysis of the three-variable model will be presented elsewhere.[15] Here we limit ourselves to presenting an example of choice of sets of values of the parameters for which the asymptotic pattern is qualitatively identical to that observed in our experiments. To obtain the pattern LS_2s_{11}, the following values of the parameters were used: $a = 0.081$, $v_1 = 10.0$, $v_2 = 11.0$, $v_3 = 20.0$, $a = 150$, $b = 434.0$, $b_1 = 3.714$, $b_2 = 21.75$, and $q = 0.1$. For these values of the parameters eqs 1−3 have three stationary states; two of them (F_1 and F_2) are unstable foci and SP is the saddle-point

$$F_1\ (u_{s1} = 146.991\,375\,8,\ v_{s1} = p_{s1} = 11.271\,152\,38) \quad (5)$$

$$\mathrm{SP}\ (u_{s2} = 74.640\,610\,63,\ v_{s2} = p_{s2} = 14.112\,448\,53) \quad (6)$$

$$F_2\ (u_{s3} = 36.344\,013\,83,\ v_{s3} = p_{s3} = 15.616\,399\,08) \quad (7)$$

In order to analyze roughly the dynamics of the system described by eqs 1−3, let us consider eqs 1 and 2 only and assume that the variable p is the parameter. For this two-variable subsystem the v-nullcline ($f(u, v) = 0$) forms an S-shaped curve on the plane (u, v) and u-nullcline ($g(u, o) = 0$) is a descending line given by $v = (b - b_1 p - u)/b_2$. It is easy to see that the S-shaped nullcline for v is given by $u = (v - v_1)(v - v_2)(v - v_3) + a$ and that its upper and lower branches are attracting whereas the middle branch is repelling. The nullclines can have one or three intersections depending on the "parameter" p. At high values of p a single steady state (SS_3) (close to F_2) exists on the lower branch of the S-shape nullcline. Decreasing p gives three steady states (SS_1, SS_2, SS_3) through a saddle-node bifurcation. SS_2 is always a saddle point, which is positioned close to SP. SS_1 lies close to F_1 on the upper branch of the S-shape nullcline, and SS_3 may be of stable or unstable focuses.

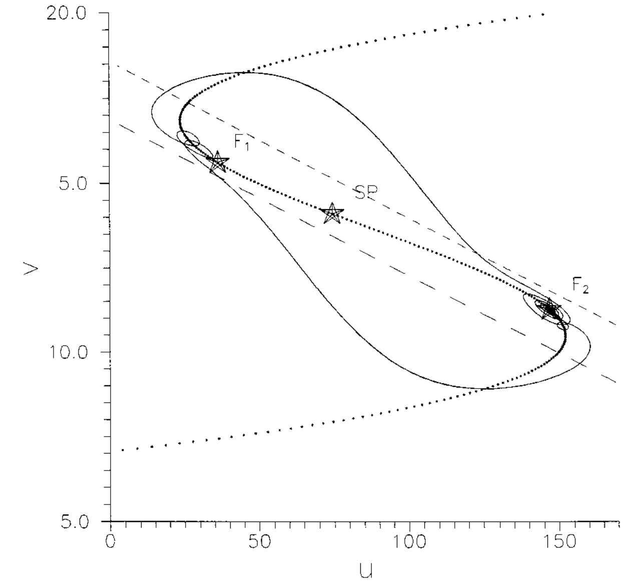

Figure 2. Projections on the phase subspace (u, v) of the nullcline for v (the point line) and two different positions of the nullcline for u (the dashed lines) corresponding to the maximal and minimal values of p for the model (1)−(3) together with the projection of the LS_2s_{11} limit cycle (solid line) on the same plane. The parameters have the following values: $\alpha = 0.081$, $v_1, = 10.0$, $v_2, = 11.0$, $v_3 = 20.0$, $a = 150$, $b = 434.0$, $b_1 = 3.714$, $b_2 = 21.75$, and $q = 0.1$. Positions of the stationary states for the three-variable system are marked by stars.

Further decreasing p causes steady states SS_3 and SS_2 to disappear through another saddle-node bifurcation, and the steady state SS_1 (close to F_1) on the upper branch of the v-nullcline remains a sole attractor. This picture of bifurcations of the reduced two-variable system allows one to explain the main features of the three-variable model. According to eq 3 the variable p follows the variable v. If p is large, then v must fall down to the lower branch of its nullcline, and "vice versa" if p is small, then v must grow up to the upper branch of its nullcline. As a matter of fact, it is not necessary that at extremal values of p the nullclines for v and u have single intersection points. They may intersect in three points. It is sufficient that at a minimal value of p the stationary state SS_3 is repelling whereas at a maximal value of p the point SS_1 is unstable. Projections on the phase subspace (u, v) of S-shaped $f(u, v) = 0$ together with two positions of linear $g(u, v, p_{min}) = 0$ and $g(u, v, p_{max}) = 0$ are shown in Figure 2. In the same figure the projection of the limit cycle corresponding to the pattern LS_2s_{11} is also shown. At proper values of the parameters a trajectory can rotate around F_1 as well as F_2, and in this way desired numbers of small peaks in a pattern can appear. A number of rotations around F_1 defines the value of n (equal to 2) in the LS_ns_m whereas a number of rotations around F_2 gives m, which is equal to 11 for the pattern discussed here. In Figure 3 numerical solution to eqs 1−3 for $v(t)$ showing the pattern LS_2s_{11} are presented. Changing the parameters in proper ranges one can obtain rich variety of new type mixed-mode oscillations.

IV. Conclusions

The example of the new type of mixed-mode oscillations described in this paper show that additional efforts should be made in order to explain them on the level of realistic chemical models. Our model seems to be the simplest one in which such complex periodic as well as chaotic oscillations are possible. It is noteworthy that only one equation is nonlinear, whereas the two remaining ones are linear. The model does not correspond to any real chemistry in the B−Z system. However, some qualitative correspondence between the variables of the model and, most importantly, variables in the B−Z reaction can be suggested. The variable v can be treated as an autocatalytic reagent and therefore should correspond to $HBrO_2$ in the B−Z chemistry. The variable u is involved in a "negative feedback" and therefore should be related to Br^-, and the variable p can be related to the concentration of the catalyst.

As a matter of fact it is not excluded that similar mixed-mode oscillations can be obtained in the Oregonator[16] and for other three-variable models suggested for description of various oscillations in the B−Z system.[17,18] Large amplitude oscillations in the Oregonator model appear in the same way as in our model. To model the complex periodic oscillations shown in this paper, it is necessary to assure rotations of a trajectory around two apparent focuses that could appear in the models mentioned above for properly chosen values of the parameters.

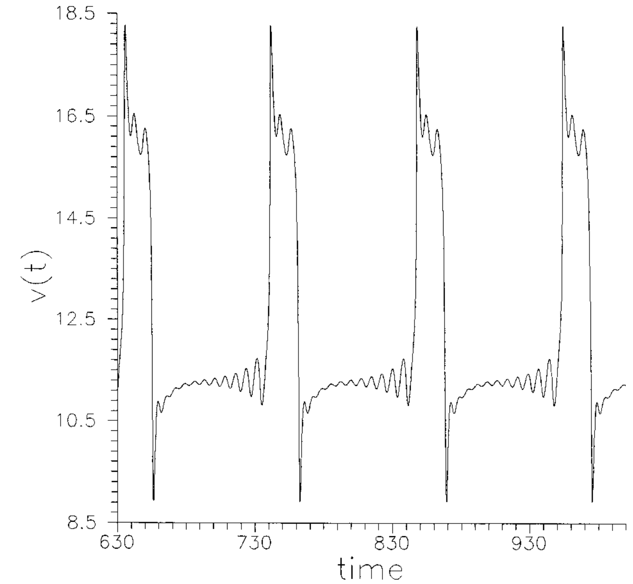

Figure 3. Asymptotic time oscillations of the variable $v(t)$ for the model (1)−(3). The parameters in eqs 1−3 are the same as in Figure 2. The pattern LS_2s_{11} is clearly visible.

References and Notes

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