Regularities in Complex Transient Oscillations in the Belousov−Zhabotinsky Reaction in a CSTR

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The Belousov−Zhabotinsky reaction (bromate−malonic acid−ferroin) exhibits regular sequences of complex (large and small amplitude) transient oscillations in a CSTR as well as in a batch reactor. General features of the dynamics in both type experiments are explained in a qualitative way using a simple model proposed recently for batch conditions.

Introduction

Various oscillations of reagents concentrations in time have been observed in chemical systems.[1−4] The best studied example is the Belousov−Zhabotinsky (BZ) reaction in which organic reagents are oxidized by bromate in the presence of metal ions as catalyst.[1−5] Simple and complex periodic oscillations as well as chaotic behavior can be observed if this reaction occurs in a continuously stirred tank reactor (CSTR).[6−8] Such oscillations have been observed in asymptotic regimes. Any dynamical system needs a certain interval of time to attain an attractor if initial concentrations are not equal to values corresponding to the attractor. There appears a transient behavior in which a system evolves from the initial concentrations to their asymptotic values. The transient behavior may contain important information about a mechanism of chemical reactions, especially in cases where oscillations in transient regimes are qualitatively different from those for asymptotic ones. For example, in an asymptotic regime one can observe periodic oscillations consisting of large amplitudes only, whereas oscillations with large as well as small amplitudes can be observed in a transient regime. Such complex oscillations in transient regimes are studied in the present paper.

As a matter of fact, oscillations in the BZ reaction for the first time were observed in a batch reactor (closed system) but they exist only during a finite interval of time after which a system approaches chemical equilibrium.[1,2,5] Usually just after the reagents are mixed a "transient regime" appears which is followed by a number of almost regular oscillations which decay after a long time. Different types of this "transient" behaviors have been observed in the BZ systems. An "induction period" was observed if malonic acid is used as organic compound of the BZ reaction.[1,9] Irregular mixtures of large- and small-amplitude oscillations (so-called double peak oscillations) were found in the BZ if ferroin was used as the catalyst.[10−12] Recently, some regularities in "transients" have been reported. "Transient period doubling" has been observed in the BZ system catalyzed by ferroin[13] and cerium.[14] "Transient period adding" has been observed in the BZ reaction catalyzed by ferroin if the initial malonic acid (MA) concentration was varied[15] and various sequences of large-amplitude oscillations followed by small ones if the initial ferroin concentration was changed.[16]

One can expect that the regularities in the transient behavior will appear also in CSTR experiments for initial concentrations identical to those for the batch experiments. The aim of the present paper is to compare experimental results showing regularities in transient behavior in a batch reactor with expected regularities in a CSTR in the bromate−MA−ferroin−H_2SO_4 system. The CSTR experiments were performed at small flow rates of reactants to ensure conditions close to the batch experiments. Batch experiments were performed for selected values of catalyst concentrations. Next, experiments in a CSTR at concentrations of the reagents in inflows equal to initial concentrations of the reagents in the batch experiments were performed. The regularities in oscillation sequences observed in both experiments are discussed on a basis of the qualitative model proposed recently[16] for the batch experiments to explain general features of the regularities in the complex dynamics in transient regimes.

Experimental Section

Reagents. Analytical grade chemicals $KBrO_3$, H_2SO_4, phenanthroline ("POCh" S. A. Gliwice), and malonic acid (Aldrich) were used without further purification and $FeSO_4\cdot 7H_2O$ was synthesized by the authors. Aqueous ferroin solution was prepared according to the standard method.[17] All solutions were prepared by using double distilled water.

Apparatus. Measurements were carried out in two reactors: a batch reactor (closed system) and a CSTR at a temperature of 21 °C, which was measured inside the reactors. In both cases the total volume of the reaction mixture was 40 cm^3 and the stirring rate was 500 rpm. The diameter of both reactors was 4.2 cm. In CSTR experiments 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 for ferroin and bromate solutions. The state of the system was followed by simultaneous measurements of potentials of platinium and bromide electrodes using a saturated calomel reference 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.

Procedures. In batch experiments the reaction was initiated by adding the ferroin solution to the mixture of $KBrO_3$, MA, and H_2SO_4. In all experiments the initial concentrations of $KBrO_3$, MA, and H_2SO_4 were identical and equal to $[KBrO_3]$

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TABLE 1: Changes of LS_i Patterns with Initial Ferroin Concentration in Batch and CSTR Experiments

ferroin, M × 10^{-3}	batch pattern	lifetime, s	CSTR pattern	lifetime, s
0.75	$(LS_3)2(LS_2)4(LS_1)$	360	$(LS_3)2(LS_2)6(LS_1)$	440
0.88	$(LS_3)2(LS_2)4(LS_1)$	396	$(LS_3)2(LS_2)6(LS_1)$	428
1.07	$(LS_3)2(LS_2)5(LS_1)$	456	$(LS_4)(LS_3)2(LS_2)6(LS_1)$	597
1.125	$(LS_3)2(LS_2)5(LS_1)$	401	$(LS_4)(LS_3)2(LS_2)6(LS_1)$	544
1.25	$(LS_4)2(LS_2)5(LS_1)$	540	$(LS_4)(LS_3)2(LS_2)5(LS_1)$	548
1.88	$(LS_4)(LS_3)2(LS_2)4(LS_1)$	608	$(LS_4)(LS_3)2(LS_2)6(LS_1)$	740
2.06	$(LS_4)(LS_3)2(LS_2)3(LS_1)$	544	$(LS_4)(LS_3)2(LS_2)5(LS_1)$	651
2.19	$(LS_4)(LS_3)(LS_2)3(LS_1)$	420	$(LS_5)(LS_3)2(LS_2)4(LS_1)$	572
2.81	$(LS_4)(LS_3)(LS_2)3(LS_1)$	472	$(LS_5)(LS_3)2(LS_2)4(LS_1)$	520
3.13	$(LS_4)(LS_3)(LS_2)2(LS_1)$	468	$(LS_5)(LS_3)2(LS_2)3(LS_1)$	544
3.44	$(LS_4)(LS_3)(LS_2)(LS_1)$	476	$(LS_5)(LS_3)(LS_2)3(LS_1)$	540

= 0.19 M, [MA] = 0.68 M, and $[H_2SO_4]$ = 0.32 M. The concentration of ferroin was varied in the range: 7.5×10^{-4} to 3.44×10^{-3} M.

The potentials of the electrodes were usually recorded after mixing of the reactants up to a moment of time when sequences of LS_i peaks decayed and then the system exhibited almost regular large-amplitude oscillations. In some cases the measurements were continued for a long time during which the system had exhibited many (hundreds) almost regular large-amplitude oscillations.

The mixture of the reagents prepared in the batch reactor was immediately poured into the CSTR and simultaneously the peristaltic pump was switched on. As small as possible values of inflows of the reagents were used: 0.1 cm^3/min for ferroin, 0.1 cm^3/min for a mixture of malonic acid with H_2SO_4, and 0.4 cm^3/min for $KBrO_3$. The concentrations of the reagents in the flows were chosen in such a way that their concentrations after mixing were identical to the initial concentrations in the corresponding batch experiment. A period of time from the moment of mixing of all reagents until the registration of the first LS_i sequence was about 2 min. This time was practically the same as in the batch type experiments.

Results

Experimental Results. In order to compare the reproducibility of the results of batch experiments presented in the paper[16] we repeated the experiments for the chosen initial concentrations of ferroin but for a little lower temperature (21 °C instead of 22.3 °C). Typical transient oscillations of Pt and Br electrodes potentials are shown in Figure 1a,b. The sequence of large amplitude (L) followed by various numbers of small amplitude (S) oscillations is clearly visible. Next the system exhibits a number of almost regular large-amplitude oscillations. After some time these oscillations decay and the system attains equilibrium. The LS_i sequences observed at various initial concentrations of ferroin are shown in Table 1. In most cases the patterns are a little richer than those obtained previously.[16] The regularities in transients appear in some range of temperature only[16] and are sensitive to the temperature. Therefore, the differences in patterns seem to be caused by the fact that the present experiments were performed at 21 °C whereas the previous ones[16] at 22.3 °C. Additionally, it is not excluded that the differences come from impurities present in chemicals used in both experiments. It is noteworthy that the present experiments confirm the appearance of regularities in transient oscillations in a batch reactor.

Typical transient oscillations of Pt and Br electrodes potentials for CSTR experiments are shown in Figure 2a,b. The sequence of large-amplitude (L) followed by small-amplitude (S) oscillations appears. Next, the system, being still in the transient regime, exhibits large-amplitude oscillations and after some time an asymptotic regime is reached in which the system oscillates periodically with large-amplitude oscillations. The LS_i sequences observed at various concentrations of ferroin are also shown in Table 1.

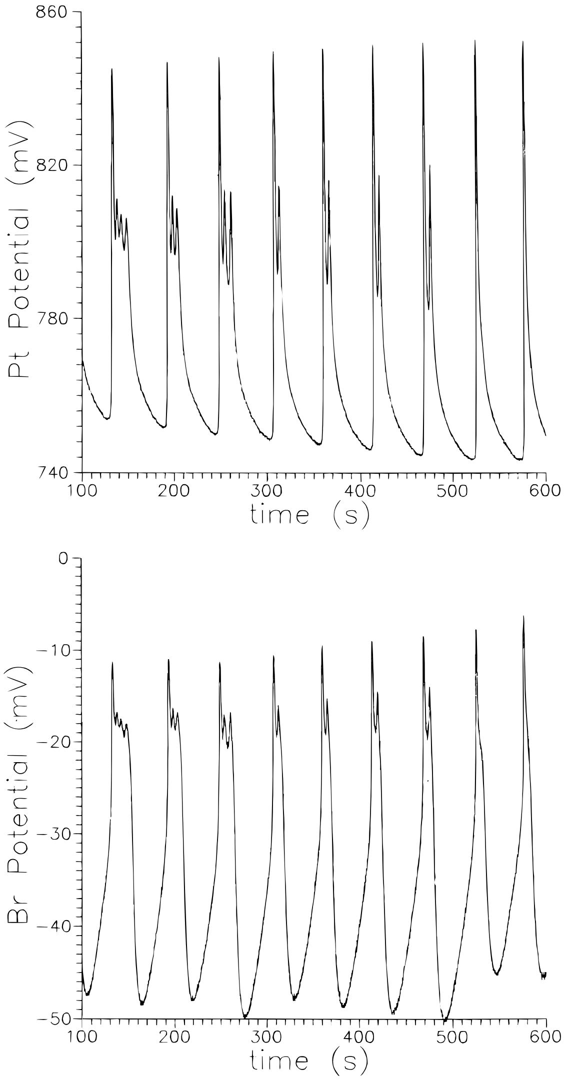

Figure 1. Time oscillations of potentials of Pt (a, top) and Br (b, bottom) electrodes in the batch experiment for the initial concentrations of ferroin = 0.000 88 M. The transient pattern $(LS_3)2(LS_2)4(LS_1)$ is shown together with two large-amplitude oscillations.

The patterns obtained in the CSTR experiments are richer than those in the batch ones. The CSTR patterns consist of more LS_i peaks or more S in LS_i peaks as compared with the batch patterns (see Table 1). Each pattern in both experiments is characterized by the following features: (i) the number of small oscillations decreases in subsequent LS_i peaks; (ii) the minimal values of potentials between small oscillations decrease in each LS_i peak; and (iii) the amplitudes of small oscillations in the LS_i peaks increase in each sequence.

In all cases investigated here "lifetimes" of LS_i patterns (the period of time from a beginning of the first LS_i peak to end of the last LS_i one) in CSTR experiments were longer than in the batch ones (see Table 1).

Both types of experiments were repeated several times for all concentrations of ferroin. The LS_i patterns were reproducible in the sense that identical patterns were observed in most repetitions. Sometimes the observed patterns differed by one S. Lifetimes of LS_i sequences varied in a range of 10% in both types of experiments.

Qualitative Model. The transient LS_i oscillations observed in both types of experiments as well as in other ones[15,16] can be described in a qualitative way by the four-variable dynamical model presented recently.[16] The model consists of four differential equations:

$$dv/dt = \alpha[u - (v - v_1)(v - v_2)(v - v_3) + a] = \alpha f(v,u) \quad (1)$$

$$du/dt = b_1(c_1 - c_2 p) - b_2 v - u = g(v,u,p) \quad (2)$$

$$dp/dt = q(v - p) = h(v,p,q) \quad (3)$$

$$dq/dt = -\gamma(q - q_1) = k(q) \quad (4)$$

where v, u, p, and q denote variables which imitate concentrations of reagents, t is time, and the remaining symbols denote parameters.

A general concept of the model is as follows (for details see reference[16]). The nullcline for v ($f(v,u) = 0$) has an S shape on the phase plane u, v. The lower and the upper branches of the nullcline are attracting whereas the middle branch is repelling. The nullcline for u ($g(v,u,p) = 0$) is a straight line and its position on the plane u,v is controlled by the actual value of the variable p. There is a range of values of p in which the nullclines intersect at three points: SS_1, SS_2, and SS_3. SS_1 and SS_2 lie on the repelling branch of the nullcline for v, whereas SS_3 is on the lower attracting branch. The SS_2 is always a saddle point whereas SS_1 is a focus which is usually unstable but can be stable if it is close to the upper branch and the variable v is sufficiently slow. If the variable p grows, the nullcline for u shifts down and at some value of p the points SS_1 and SS_2 disappear due to a saddle-node bifurcation and for sufficiently large values of p the point SS_3 lying on the lower branch of the curve $f(v,u) = 0$ becomes a sole attractor. If the variable p falls, the nullcline for u moves up and at some other value of p the points SS_3 and SS_2 disappear due to another saddle-node bifurcation and SS_1 remains an attracting point for the u,v subsystem.

Let us note that according to eqs 1−2 if p is small (the nullcline for u is shifted up), the variable v must grow to values close to the upper branch of the S-shaped nullcline. Then according to eq 3 the variable p grows too and when its value becomes sufficiently large the nullcline for u is shifted down and the variable v must fall close to values on the lower branch of the S-shaped nullcline. Next, according to eq 3 p falls to a minimal value. In this way, switchings of positions of the nullcline for u between the upper and lower attracting branches of the S-shaped nullcline occur. Oscillations appear if at minimal value of p the nullcline for u intersects only the upper branch of the nullcline for v and at maximal value of p the both nullclines intersect at the lower branch of the S-shaped curve.

For α sufficiently large the system has a limit cycle which corresponds to large-amplitude single peak oscillations. The behavior of the system changes if the variable v becomes slower (α is small). In this case a trajectory can move around the unstable focus SS_1 before switching to the lower branch of the nullcline for v. In this way the large-amplitude oscillations followed by small-amplitude oscillations (LS_i) appear.

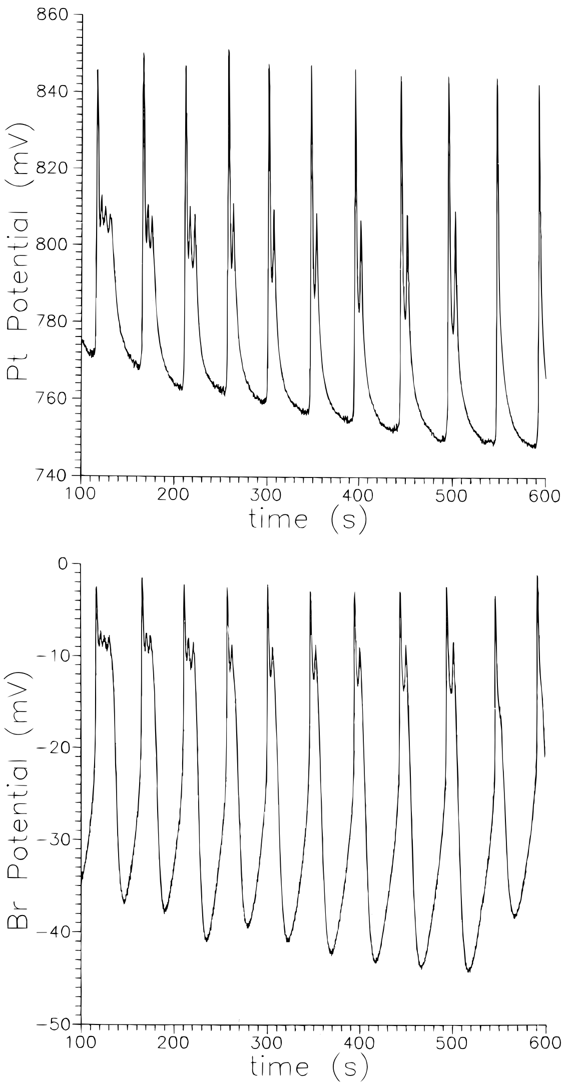

Figure 2. Time oscillations of potentials of Pt (a, top) and Br (b, bottom) electrodes in the CSTR experiments. Initial concentrations of all reactants are the same as in Figure 1. The transient pattern $(LS_3)2(LS_2)6(LS_1)$ is clearly visible together with two large-amplitude oscillations.

The number of small-amplitude oscillations is determined by an actual value of the variable q. In Figure 3 examples of limit cycles for two fixed values of q are shown. According to eq 4, the variable q grows exponentially from its initial value $q(0) = q_0$ to an asymptotic value q_1. The trajectory of the whole system (1)−(4) "winds" around the limit cycles shown in Figure 3 according to the increasing value of q and, after some sequences of LS_i oscillations, approaches asymptotic trajectory determined by q_1. For the model describing the batch experiments this asymptotic trajectory should be the stationary state corresponding to the equilibrium. This is not the case for values of the parameters given in this paper. Before the batch systems stop oscillating hundreds of large-amplitude oscillations appear and the fitting of the values of the parameters to get exact numbers of these oscillations is a delicate problem.

Choosing the appropriate values of γ, q_1, and q_0, one can obtain most of the patterns shown in Table 1 for the values of the remaining parameters given in Figure 3. The value of q_0 determines the number of small-amplitude oscillations in the first LS_i peak in a transient sequence. Decrease of q_0 leads to

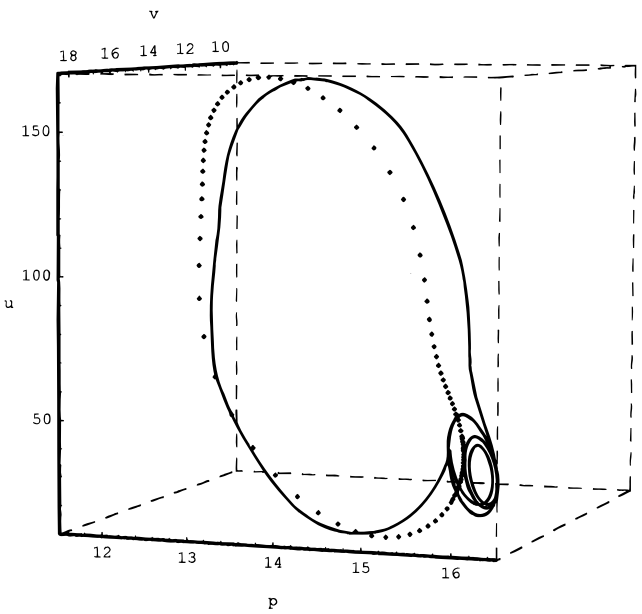

Figure 3. 3D plots of two limit cycles for three-variable model described by eqs 1−3 at two fixed values of q and the following values of the remaining parameters: $\alpha = 0.065$; $v_1 = 10$; $v_2 = 11$; $v_3 = 20$; $a = 150$; $b_1 = 377$; $b_2 = 21.7$; $c_1 = 1.158\,03$; $c_2 = 9.852\,21 \times 10^{-3}$. For $q = 0.23$ the limit cycle has the pattern LS_4 (solid line) whereas for $q = 0.29$ the limit cycle has large-amplitude oscillations (L) only (point line).

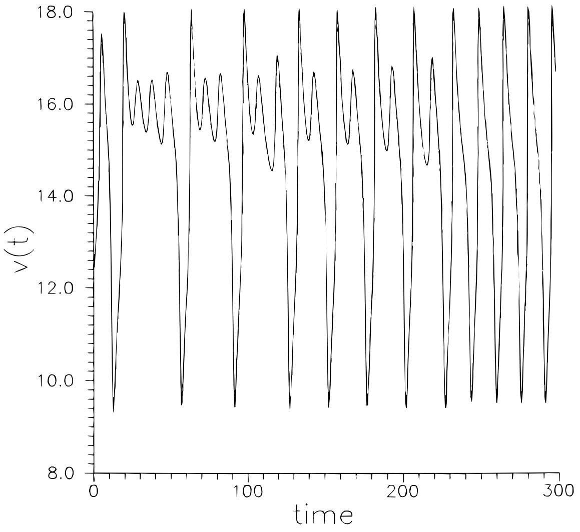

Figure 4. Transient time oscillations for the variable v in the four-variable model (eqs 1−4). The parameters in eqs 1, 2, and 3 are the same as in Figure 3. The following values of the parameters in eq 4 are chosen: $\gamma = 0.002$; $q_1 = 0.38$; $q_0 = 0.23$. The solution is obtained for the initial condition $u_0 = 150$, $v_0 = 12$, and $p_0 = 16$. The pattern $(LS_3)2(LS_2)4(LS_1)$ corresponds to the batch patterns for the initial ferroin concentration equal to 0.000 75 and 0.000 088 M (compare with Figure 1).

an increase in the number of small oscillations in LS_i peaks. The number of LS_i peaks in the patterns is controlled by γ and $q_1 - q_0$. Decreasing γ or increasing $q_1 - q_0$, one can obtain patterns with greater number of LS_i peaks. The parameter q_1 determines the form of asymptotic oscillations.

Examples of transient sequences are shown in Figures 4 and 5. The values of the parameters are chosen in such a way that there is a qualitative agreement with the experimental results shown in Figures 1 and 2.

Let us note that it is sufficient to replace values of γ or $q_0 - q_1$ chosen for the batch conditions by smaller ones in order to obtain patterns corresponding to the CSTR experiments performed at the same initial concentrations of reagents. The patterns corresponding to the CSTR experiments obtained from the model are longer in time than those for the batch ones. In all experiments (see Table 1) similar results were observed.

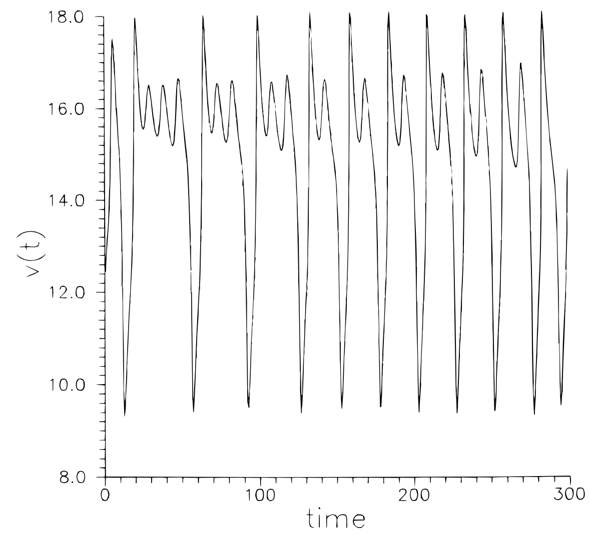

Figure 5. The same as in Figure 4: the values of all the parameters are the same as in Figure 4 but $\gamma = 0.0016$. The pattern $(LS_3)2(LS_2)6(LS_1)$ corresponds to the CSTR patterns for the initial ferroin concentration equal to 0.000 75 and 0.000 088 M (compare with Figure 2).

Moreover, we want to stress that the transient sequences obtained from the model have the same features as those observed in the experiments (i), (ii), and (iii) in the previous section for used electrodes. The decrease in the number of small oscillations in each transient pattern is the result of a monotonic change of the fourth variable q added to the three-variable model. Decrease of minimal values between small oscillations and increase of their amplitudes for the variable v are caused by "rotations" of a trajectory around the unstable focus.

Discussion

The transient LS_i patterns observed in CSTR are more rich in small amplitudes than those observed in batch conditions (see Table 1). It is not surprising because in CSTR conditions the system stays a longer time in a range of reagent concentrations which allow small-amplitude oscillations. One can expect that a gradual increase in flow rates, keeping the same concentrations in the inlets, increases the number of small oscillations. These expectations were confirmed by our preliminary experiments. At flow rates 2 times greater than those for the Table 1 and at a concentration of ferroin equal to 1.25×10^{-3} M, the observed transient pattern was $(LS_4)(LS_3)2(LS_2)8(LS_1)$ and next the system exhibited large-amplitude oscillations. If the flow rate is substantially increased, so that the residence time is equal to 4.80 min, the system with the same ferroin concentration exhibits $n(LS_4)$ pattern and the sequence (LS_4) is maintained during eight residence times that is practically in the asymptotic regime. It is noteworthy that in LS_4 patterns differences in amplitudes of large and small oscillations are similar to those shown in Figures 1 and 2, and therefore, the distinction between them is possible. One can expect that each single LS_i peak observed in a batch experiment can be found in the CSTR at proper conditions.

It is noteworthy that the qualitative properties of the system can be described by models (1)−(4). The model is formal and has no direct correspondence to the chemical mechanism of the BZ reaction. Nevertheless, the types of nonlinearities used in the model can be useful in understanding the chemical mechanism of the system. The variable v plays the role of an autocatalytic reagent and therefore should correspond to $HBrO_2$ in the BZ chemistry. The variable u describes a "negative feedback" and therefore should be related to Br^-. The variable p can be related to the catalyst concentration. The transient character of the complex oscillations is governed by a monotonic growth of the variable q that reflects the production of bromomalonic acid which is accompanied by an exhaustion of bromate and malonic acid.

As a matter of fact, large-amplitude oscillations in the Oregonator model appear in the same way as in our model.[18] Therefore, we believe that the model is useful in the qualitative description of the BZ reaction.

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