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New evidence of transient complex oscillations in a closed, well-stirred Belousov-Zhabotinsky system

LJILJANA KOLAR-ANIĆ[a*], SLAVICA BLAGOJEVIĆ[b], NATAŠA PEJIĆ[b], NEBOJŠA BEGOVIĆ[c], STEVAN BLAGOJEVIĆ[c] and SLOBODAN ANIĆ[a]

[a]Faculty of Physical Chemistry, University of Belgrade, Studentski trg 12-16, P. O. Box 137, YU-11001 Belgrade, [b]Faculty of Pharmacy, University of Belgrade, Vojvode Stepe 450, YU-11000 Belgrade and [c]Institute for General and Physical Chemistry, Studentski trg 12, YU-11000 Belgrade, Serbia (e-mail: lkolar@ffh.bg.ac.yu)

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Abstract: Some new experimental evidence of complex irregular oscillations in the Belousov–Zhabotinsky reaction realized in a batch reactor is presented. The results were obtained under relatively low cerium and malonic acid concentrations. One-dimensional maps were used for general discussion, and, particularly, for the influence of noise on the evolution of the oscillations.

Keywords: Belousov–Zhabotinsky reaction, chaotic behavior, dissipative processes, one-dimensional maps, oscillating reactions.

INTRODUCTION

It is well known that, besides simple periodic behavior,[1–9] the complex oscillations including mixed mode and chaotic ones can be found in oscillatory chemical reaction systems under defined external conditions in open and closed (batch) reactors.[10–16] In open reactors, these phenomena are obtained not only in a transient, but also in a permanent regime. Under batch conditions, only transient states are possible.

In the following, new experimental evidence of the mentioned phenomena in the Belousov–Zhabotinsky (BZ) reaction induced by the initial cerium concentration in experiments performed under well-stirred batch conditions.

Complex oscillations, including chaotic behavior, have already been mentioned in numerous publications related to the Belousov–Zhabotinsky reaction catalyzed by ferroin and cerium and carried out in an open, continuously well-stirred tank reactor (CSTR).[17–25] To the best of our knowledge, these phenomena in a well-stirred batch reactor have only been reported in a few publications.[26–33]

* Corresponding author.

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Thus, Ruoff[26,27] found chaotic behavior of a BZ reaction system under batch conditions influenced by high initial cerium (Ce(IV)) concentrations (Table I). The chaotic behavior, when it exists, was observed at the end of one run, *i.e.*, when the reaction system was near the border of its excitable steady state. (Let it be noted that in this region the concentration of malonic acid was lower than the initial one). Wang, Sørensen and Hynne[28,29] obtained period doubling, intermittency, mixed mode and quasiperiodic oscillations in a batch reactor under conditions given in Table I. In their experiments, the complex behavior was stimulated by increasing the initial cerium, bromomalonic and malonic acid concentrations and by decreasing the initial sulfuric acid concentration. The phenomena were also more expressed at the end of an oscillogram. Strizhak, Ivashchenko and Kawczinski observed mixed mode oscillations in the BZ system with ferroin (Table I).[30] Strizhak and Kawczinski[31] reported that these phenomena were only found in a defined region of initial ferroin concentrations. For lower initial ferroin concentrations than the ones given in Table I, a stable steady state was obtained, whereas at higher concentration, only regular large single-peak oscillations appeared. Johnson, Scott and Thompson obtained different kinds of complex oscillations, including transition chaotic behavior.[32] Experiments related to chaos and noise having an educational aim are presented in ref. 33.

TABLE I. The regions of the initial concentrations where complex regular and irregular or chaotic oscillations were observed. The concentrations are in mol dm^{-3}

Ref.	T/ °C	$[\text{Malonic acid}]_0$	$[BrO_3^-]_0$	$[KBr]_0$	$[H_2SO_4]_0$	$[\text{Ferroin}]_0$	$[Ce(IV)]_0$	$[Ce(III)]_0$
26,27	25	0.28–0.30	0.10		1.00		2.10×10^{-3}–2.10×10^{-2}	
28,29	25.0 ± 0.1	0.267–0.44	0.08		0.47–1.00			0.00133
30,31	22.3 ± 0.1	0.10–0.68	0.19		0.32	0.50×10^{-3}–7.50×10^{-3}		
32	25	~0.27–0.475	0.08		1.00			0.00133
New results	30.0 ± 0.1	0.032	0.063	0.00151	1.00			1.75×10^{-5}–1.00×10^{-3}

EXPERIMENTAL

The kinetics of the Belousov–Zhabotinsky oscillatory reaction was analyzed in a well-stirred closed reactor (magnetic stirrer of 700 rpm) at a constant temperature $T = 30 \pm 0.1$ °C. A glass cell Methrom EA-876-20 with a reaction volume of 51 ml was used as the reactor. The evolution of the BZ reaction was monitored potentiometrically using a Pt-electrode coupled with an Ag/AgCl reference electrode *via* a sulfate bridge.

All experiments were performed at constant values of the initial concentrations of potassium bromate, sulphuric acid, potassium bromide and malonic acid: $[H_2SO_4]_0 = 1.00$ mol dm^{-3}, $[KBrO_3]_0 =$

6.20×10^{-2} mol dm^{-3}, $[KBr]_0 = 1.50 \times 10^{-5}$ mol dm^{-3}, $[CH_2(COOH)_2]_0 = 3.20 \times 10^{-2}$ mol dm^{-3}. The initial cerium sulphate concentration, $[Ce_2(SO_4)_3]_0$, was varied from 1.00×10^{-6} to 5.00×10^{-3} mol dm^{-3}.

The introduction of 1 ml of Ce(III)-sulphate solution to 50 ml of the standard mixture of potassium bromate, sulphuric acid, malonic acid and potassium bromide solution was taken as the start of the reaction.

The reagents were of commercial analytical grade and were used without further purification. Deionized water of specific resistance $\rho = 18$ MΩ cm^{-1} was used throughout.

RESULTS AND DISCUSSION

The results of some of the studies of the mentioned phenomena in the closed Belousov–Zhabotinsky reaction system as a function of the initial cerium concentration are presented in Fig. 1. In the experiments, the initial cerium concentration, $[Ce_2(SO_4)_3]_0$, was varied from 1.00×10^{-6} to 5.00×10^{-3} mol dm^{-3}. For very low initial concentrations of cerium (less or equal to 1.00×10^{-5} mol dm^{-3}), only stable steady states were obtained. At a concentration of 1.75×10^{-5} mol dm^{-3}, sequences of stable steady states, period-1, period-2 and some kind of bursting phenomena with 4 wave-form oscillations in one experiment were observed (Fig. 1a). This bursting domain appeared between the stable steady state at the beginning of Fig. 1a and the irregular periodic behavior that emerges latter. The period-2 oscillations in the considered transient system changed their form from two asymmetric to two symmetric peaks which finally merged into only one. The numerous dynamic states and chaotic transitions between them gave the impression that the whole oscillogram was irregular. However at the end of this irregular regime, *i.e.*, when the concentration of malonic acid was lower, the periodic evolution was more regular than at its beginning. At a little higher concentration of cerium ($[Ce_2(SO_4)_3]_0 = 2.50 \times 10^{-5}$ mol dm^{-3}), the periods with regular and irregular oscillations were better divided (Fig. 1b), although, as in the previous case, at the beginning of the oscillogram bursting oscillations, but with four, five and six peaks, were found. Chaotic oscillations were obtained only during the transition between small- and large-amplitude oscillations. The number of peaks increased with time, or with decreasing malonic acid concentration. On further increasing of the initial cerium concentration (Fig. 1c, d, e and f) different mixed mode oscillations appeared. For higher initial cerium concentrations (higher than or equal to 2.50×10^{-3} mol dm^{-3}), only simple oscillations were found. Moreover, with increasing initial cerium concentration, some kinds of bursting oscillations which appear at the beginning of oscillograms presented in Fig. 1a and b disappeared and at the same place a supercritical Hopf bifurcation point appeared in Fig. 1c and 1d. This bifurcation point seems to turn into a subcritical one at higher initial cerium concentrations (Fig. 1e and f). Moreover, at any cerium concentration, the time-evolution of the system was caused by decomposition of malonic acid.

Obviously, different kinds of complex regular and irregular oscillations were found (Fig. 1). With the aim of showing the influence of noise on the experimental results, particularly on the chaotic oscillations (Fig. 1a and b), it was decided to ap-

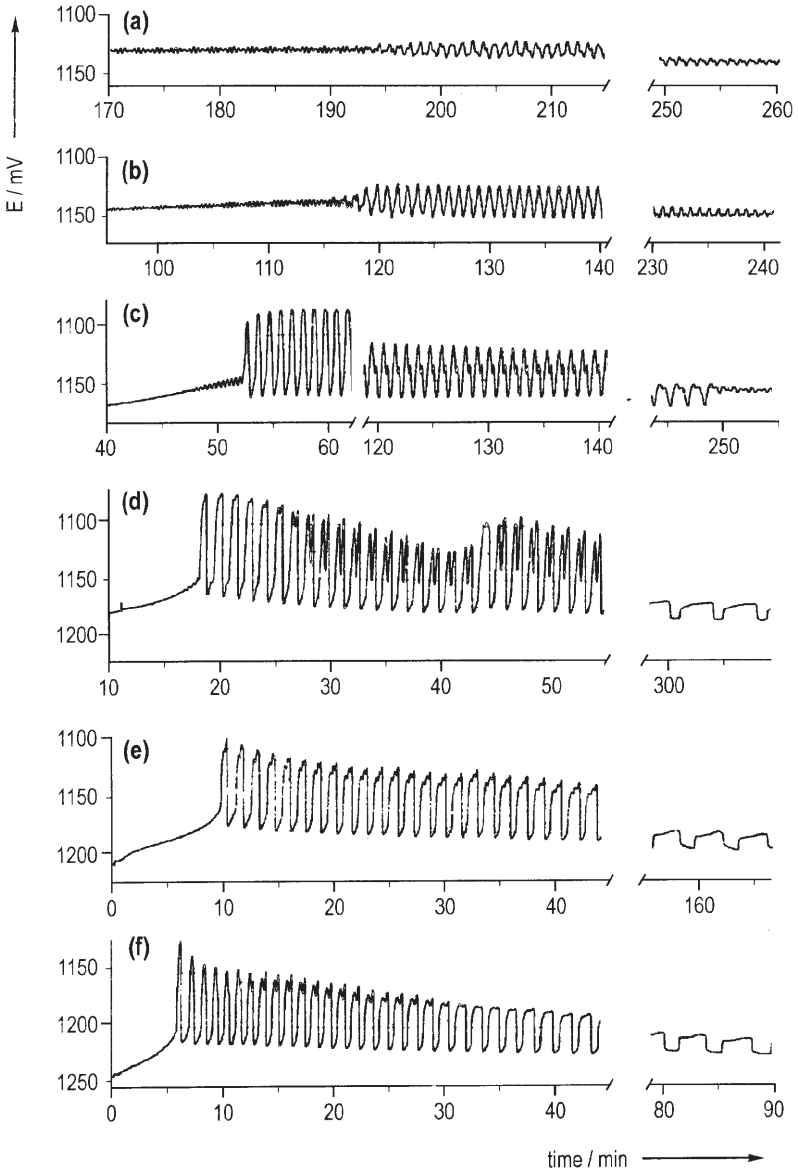

Fig. 1. The time evolution of the platinum electrode potential for the Belousov–Zhabotinsky reaction. $[H_2SO_4]_0 = 1.00$ mol dm^{-3}, $[KBrO_3]_0 = 6.20\times10^{-2}$ mol dm^{-3}, $[KBr]_0 = 1.50\times10^{-5}$ mol dm^{-3}, $[CH_2(COOH)_2]_0 = 3.20\times10^{-2}$ mol dm^{-3}. $[Ce_2(SO_4)_3]_0$ in mol dm^{-3} was varied: (a) 1.75×10^{-5}; (b) 2.50×10^{-5}; (c) 5.00×10^{-5}; (d) 1.67×10^{-4}; (e) 5.00×10^{-4}; (f) 1.00×10^{-3}.

ply One-Dimensional Map (1D map) analysis, although this method was developed for a reaction system in the permanent regime (CSTR).[12–16] The 1D maps obtained by presenting successive oscillatory minima, which correspond to successive potential maxima (see Fig. 1), are given in Fig. 2.

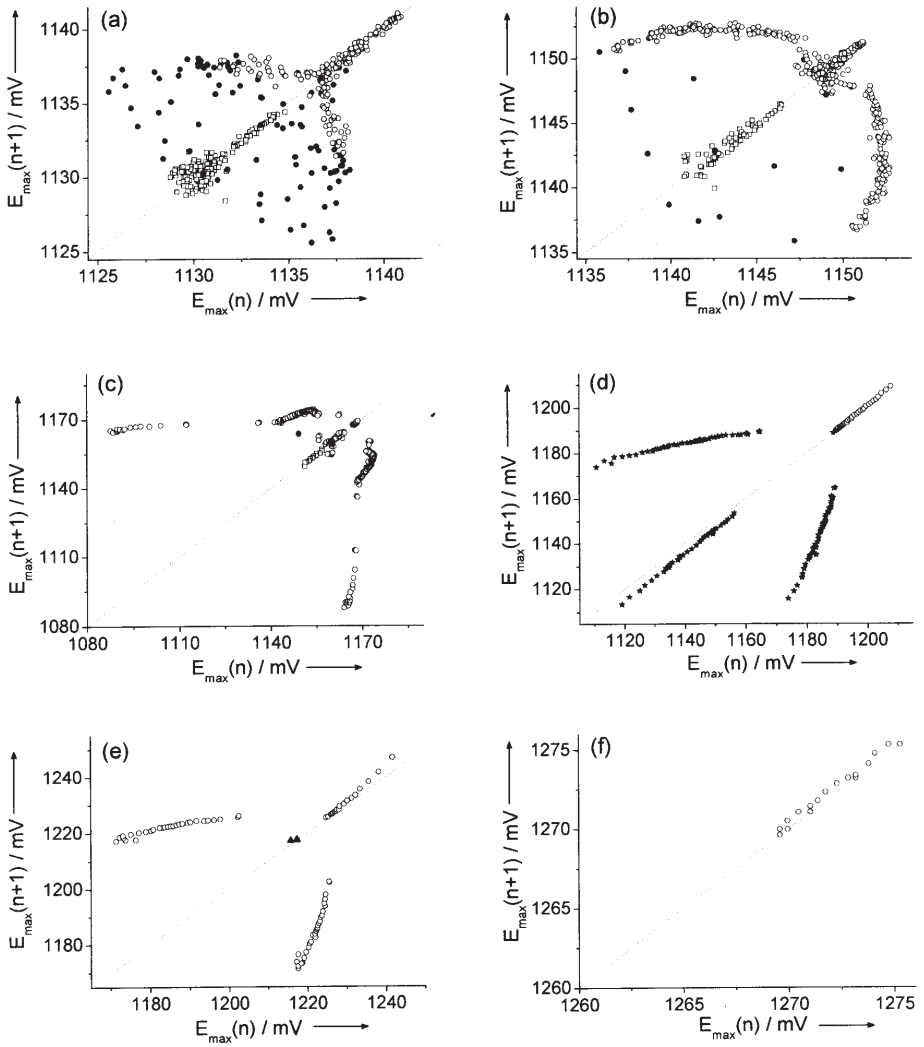

Fig. 2. The 1D maps obtained by presenting the successive oscillatory minima which correspond to successive potential maxima of the platinum electrode. $[Ce_2(SO_4)_3]_0$ in mol dm^{-3} was varied: (a) 1.75×10^{-5}; (b) 2.50×10^{-5}; (c) 5.00×10^{-5}; (d) 5.00×10^{-4}; (e) 1.00×10^{-3}; (f) 2.50×10^{-3}. The concentrations of the other species were the same as in Fig. 1. Note that the scales of the coordinates in Figures (a)–(c) are different. For details of the symbols, see the text.

Before any discussion it should be noted that Fig. 2a, b and c correspond to Fig. 1a, b and c, whereas Fig. 2d and e correspond to Fig. 1e and f. In Fig. 2f the concentration of cerium was the highest one. The one-dimensional map of the case presented in Fig. 1d is similar in the form to the map 2d.

Analyzing the 1D maps, it can be seen that the largest disorder of points is found in the case with the lowest initial cerium concentration which produces any oscillatory behavior (Fig. 2a). In this case, the noise has the most important influ-

ence on the oscillatory time evolution of the system, particularly on the large-amplitude oscillations (full cycles). The small-amplitude oscillations at the begining of the oscillatory behaviour (squares) and its end (cycles) are more regular, although complex. At all higher initial concentrations of cerium, a more regular time evolution is evident (Fig. 2b–f). Several disordered points in Fig. 2b (full cycles) are due to the chaotic behavior in the transition from small- to large-amplitude oscillations, whereas one point in the total disorder in Fig. 2c (full cycle) denotes the abrupt transition between them. The mixed mode oscillations with one large- and one small-amplitude oscillation (LS) in Fig. 2c produce approximately symmetric branches with respect to the diagonal. Three slightly asymmetric branches in Fig. 2d (full stars) are due to LS_2 oscillations presented in Fig. 1e. The cycles in the same figure denote the regular oscillations at the end of the oscillogram. Obviously, increasing the initial cerium concentration shifts the maps toward an approximately diagonal form. This corresponds to the dynamic state with regular oscillations (LS_0) and a minor potential shift of the oscillatory minima obtained when $[Ce_2(SO_4)_3]_0 \geq 2.50 \times 10^{-3}$ mol dm^{-3} (Fig. 2f). Several asymmetric points with respect to the diagonal in the case given in Fig. 2e appear because of an abrupt increase of the potential maxima characteristic for the last regular oscillations. The full triangles in the same figure are due to the first three simple oscillations.

Hence, the initial cerium concentration can be considered as the bifurcation parameter for the analyzed system under the considered conditions. Moreover, in every experimental run where different kinds of oscillations appeared, the regularity was also caused by the malonic acid concentration, which decomposes during the reaction. The chaotic and mixed mode oscillations (if they exist), appeared at the beginning of the reaction, when the malonic acid concentration was relatively higher than at the end of the oscillatory domain. A similar conclusion was obtained when ferroin was taken as the metallic catalyst.[31] In both cases, this is probably due to the relatively very low initial malonic acid concentration (Table I), so that the system at the beginning of the oscillatory state was at the end of the region with irregular oscillations. In references 26–29 and 31, when the initial malonic acid concentration was higher, chaotic behavior was obtained at the end of the oscillatory evolution. Hence, this is only an apparently opposite influence of the malonic acid concentration due to the different initial conditions. In fact, our initial malonic acid and cerium concentrations were very low with respect to the other cases where complex oscillations and chaotic behaviors were found. Thus, one new point in the region with complex irregular oscillations is presented (Table I).

CONCLUSION

Analyzing the obtained results, several points can be emphasized.

* The influence of noise at low cerium and malonic acid concentrations is very important.

* The influence of noise on the large-amplitude oscillations is more important than it is on the small-amplitude oscillations obtained in the transition regions between the stable steady states and the large-amplitude oscillations.

* The type of oscillations and their evolution is very well illustrated by 1D maps of the potential maxima.

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ИЗВОД

НОВОЗАБЕЛЕЖЕНЕ ТРАНЗИЈЕНТНЕ КОМПЛЕКСНЕ ОСЦИЛАЦИЈЕ У ЗАТВОРЕНОМ БЕЛОУСОВ-ЖАБОТИНСКИ РЕАКЦИОНОМ СИСТЕМУ СА ДОБРИМ МЕШАЊЕМ

ЉИЉАНА КОЛАР-АНИЋ[а], СЛАВИЦА БЛАГОЈЕВИЋ[б], НАТАША ПЕЈИЋ[б], НЕБОЈША БЕГОВИЋ[в], СТЕВАН БЛАГОЈЕВИЋ[в] и СЛОБОДАН АНИЋ[а]

[а]*Факултет за физичку хемију, Универзитет у Београду, Студентски трг 12-16, п.пр. 137, 11001 Београд,* [б]*Фармацеутски факултет, Универзитет у Београду, Војводе Степе 450, 11000 Београд и* [в]*Институт за општу и физичку хемију, Студентски трг 12, 11000 Београд*

Дају се нови експериментални резултати о комплексним нерегуларним осцилацијама БЖ система оствареног у затвореном реактору, у условима релативно ниске концентрације церијума и малонске киселине. Једнодимензионалне мапе су коришћене за генералну дискусију резултата, а посебно за утицај шума на осцилаторну еволуцију.

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