STUDY OF SELF OSCILLATORY BELOUSOV–ZHABOTINSKY SYSTEMS UNDER THE PERTURBATION OF EXTERNAL EMF

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An examination of the current and potential oscillations in the self oscillatory Belousov–Zhabotinsky system under the application of external EMF is presented for the first time. The system involves Mn(II) as the metal ion catalyst and malic acid/citric acid/malonic acid as the substrate. External EMF shifts the oscillatory profile to the higher potential range by the magnitude of applied EMF. The amplitude of current oscillations increases with the magnitude of external EMF. The behaviour of the system with and without a complexing agent (tetrasodium pyrophosphate) is rationalised in terms of individual steps involved in the overall reaction.

Key words: Belousov–Zhabotinsky reaction; Perturbation by external EMF; Current oscillations; Potential oscillation.

Oscillatory reaction in the Belousov–Zhabotinsky (B–Z) and Briggs–Rauscher (B–R) systems has been investigated employing different experimental techniques[1–3]. The oscillatory behaviour of systems involving the dissolution of metal in a suitable medium has also been presented and discussed[4] as well as a detailed investigation of the B–Z and B–R systems employing the potentiometric followup of the reaction[5,6]. A critical examination of the current and potential oscillations at different compositions of the reaction mixture provided valuable information regarding the course of the reaction[7]. The resulting conclusions have been discussed in the light of the generally accepted mechanism of oscillatory systems[8,9]. Chaotic and aperiodic oscillations have been reported for the B–Z system with malonic acid as the substrate[10].

In this paper we present the study of current and potential oscillations in self oscillatory B–Z system under the application of an external EMF. The oscillatory behaviour of the system with malic acid, citric acid or malonic acid as the substrate and Mn(II) as the catalyst is presented.

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EXPERIMENTAL

Experiments were carried out under batch conditions. All the chemical used were of analytical grade and used without further purification. Sulfuric acid, malic, citric or malonic acid, and catalyst were used from the stock solution. The solution was kept well stirred and thermostatted at 30 ± 0.1 °C in a polythene beaker. In this solution an external EMF of 100 and 200 mV was applied between two platinum foil electrodes from a DC power source. The addition of potassium bromate as the last component triggered off the oscillations. Batch conditions were maintained whereas no extra component was added during the experiment. The total volume of the solution including the last component was kept constant at 25 ml in all experiments. Current and potential oscillations of the system were recorded simultaneously under the same experimental conditions by an *X*–*t* recorder (Siemens Compensograph).

While potential oscillations were recorded between the platinum or Br^- selective electrode and a saturated calomel electrode (SCE), current oscillations were recorded between two platinum foil electrodes with the area of 80 mm^2 and an inter electrode distance of 5 mm.

RESULTS AND DISCUSSION

Malic Acid–Bromate System

The current and potential oscillations of malic acid–bromate system under the conditions indicated in Table I are characterised by a frequency of 0.93 min^{-1}. The potential response of the platinum electrode is given by the relative magnitude of the exchange

TABLE I

Current (*I*) and potential (*E*) oscillatory behaviour of malic acid; system: 0.05 M $KBrO_3$, 1.0 M H_2SO_4, 0.05 M malic acid, 0.005 M $MnSO_4$; temperature 30 ± 0.1 °C

Measurement	External EMF V	Frequency of oscillations min^{-1}	Base value	Peak value	Amplitude	Wave number	Duration of oscillations min
E	0	0.93	0.780 V	0.940 V	0.160 V	1.08	21.5
I	0	0.93	0 μA	5 μA	5 μA	1.08	21.5
E	0.100	0.90	0.880 V	1.040 V	0.160 V	1.12	29.0
I	0.100	0.90	10 μA	67.5 μA	57.5 μA	1.12	29.0
E	0.200	0.90	0.980 V	1.140 V	0.160 V	1.12	29.0
I	0.200	0.90	20 μA	100 μA	80 μA	1.12	29.0
E (with 0.005 M TSPP)	0.100	0.71	0.840 V	1.000 V	0.160 V	1.40	21.0
I	0.100	0.71	20 μA	70 μA	50 μA	1.40	21.0

current density and the concentration ratio of redox couples involved. Since the values of exchange current density of both Mn(III)/Mn(II) and Br_2/Br^- redox couples are comparable (10^{-5} A cm^{-2}), the potential will be driven by the concentration ratio of two redox couples. The potential range of oscillations 0.780–0.940 V *vs* SCE indicates contribution from both the redox couples *i.e.* for Mn(III)/Mn(II) E^0 = 1.27 V and for Br_2/Br^- E^0 = 0.82 V *vs* SCE. The potential range of the right side shoulder observed in the oscillatory profile recorded with the platinum electrode at 0.780–0.820 V *vs* SCE is close to the E^0 value of Br_2/Br^- redox couple. Apparently it corresponds to the contribution from Br_2/Br^- redox couple. The higher potential range of oscillations is driven by Mn(III)/Mn(II) redox couple. This observation is further supported by the simultaneous recording of potential oscillation by platinum and bromide selective electrodes as shown in Fig. 1. The shoulder portion of the oscillations recorded with platinum electrode (Fig. 1a) exactly matches with the downward portion of the oscillations recorded with Br^- selective electrode (Fig. 1b). In case of current oscillations one cannot differentiate the right side shoulder as in the case of potential oscillations. However, this is possible by means of the application of external EMF between the two platinum electrodes. External EMF increases the amplitude of the current oscillations by enhancing the production of bromine as well as the oxidised form of the metal ion involved in the following reactions.

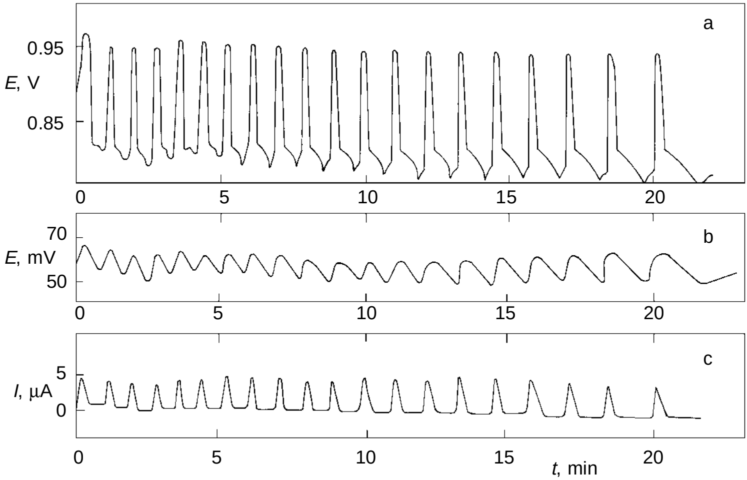

FIG. 1

Oscillatory behaviour of malic acid–bromate system. Concentration conditions: 0.05 M $KBrO_3$, 1.0 M H_2SO_4, 0.05 M malic acid, 0.005 M $MnSO_4$. Potential oscillations (*E*) recorded using a Pt electrode; b Br^- selective electrode *vs* SCE; c current oscillations (*I*) monitored using two Pt foil electrodes *vs* time *t*

$$\mathrm{HBrO_2 + Br^- + H^+ \rightleftharpoons 2\,HOBr} \tag{1}$$

$$\mathrm{HOBr + Br^- + H^+ \rightleftharpoons Br_2 + H_2O} \tag{2}$$

$$\mathrm{HBrO_2 + BrO_3^- + H^+ \rightleftharpoons 2\,BrO_2^\bullet + H_2O} \tag{3}$$

$$\mathrm{BrO_2^\bullet + Mn^{\mathit{n}+} + H^+ \rightleftharpoons HBrO_2\ M^{(\mathit{n}+1)+}} \tag{4}$$

The influence of external EMF on the amplitude of current oscillations as well as on the amplitude of the shoulder is shown in Figs 2 and 3. Initially, the amplitude of oscillations is very large. However, the system stabilises after about five minutes and its amplitude tends to decrease gradually. This contrasts with the behaviour of the system without the application of external EMF characterised by uniform amplitude of oscillations. In the case of potential oscillations, however, the application of an external EMF shifts the oscillatory profile by the magnitude of applied EMF. The influence of complexing agent has also been studied. Addition of tetrasodium pyrophosphate (TSPP) as the complexing agent stabilises both Mn(II) and Mn(III) to different extents. Therefore both base and peak potentials persist for a longer time which results in a decrease of the oscillation frequency. The addition of TSPP increases the amplitude of

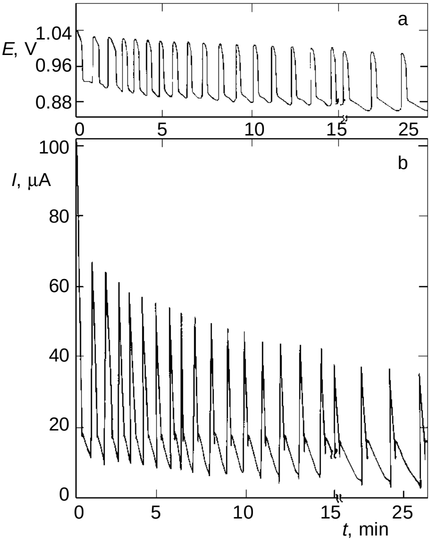

FIG. 2

Oscillatory behaviour of malic acid–bromate system under the application of 100 mV external EMF. Concentration conditions: 0.05 M $KBrO_3$, 1.0 M H_2SO_4, 0.05 M malic acid, 0.005 M $MnSO_4$. a Potential oscillations (*E*) recorded using Pt electrode *vs* SCE; b current oscillations (*I*) measured between two Pt foil electrodes *vs* time *t* the shoulder which is predominantly controlled by Br_2/Br^- (Fig. 4). Due to the presence of TSPP, step 4 is suppressed and consequently steps 1 and 2 become predominant. Increased production of bromine is in turn responsible for the increase of the right side shoulder amplitude.

Citric Acid–Bromate System

The current and potential oscillatory profiles of citric acid system under the concentrations given in Table II are characterised by a frequency of 1.87 min^{-1}. Their potential range of 0.600–0.840 V *vs* SCE indicates a mixed control by both the redox couples Mn(III)/Mn(II) and Br_2/Br^-. The potential range of citric acid system is lower compared to that of the malic acid system. This can be well understood in terms of the following steps involved in the overall reaction:

TABLE II
Current (*I*) and potential (*E*) oscillatory behaviour of citric acid; system: 0.05 M $KBrO_3$, 1.0 M H_2SO_4, 0.05 M citric acid, 0.005 M $MnSO_4$; temperature 30 ± 0.1 °C

Measurement	External EMF V	Frequency of oscillations min^{-1}	Base value	Peak value	Amplitude	Wave number	Duration of oscillations min
E	0	1.85	0.600 V	0.840 V	0.240 V	0.54	15.0
E	0.100	1.89	0.700 V	0.940 V	0.240 V	0.53	17.0
I	0.100	1.89	12.5 μA	67.5 μA	55 μA	0.53	17.0
E	0.200	1.89	0.800 V	1.040 V	0.240 V	0.53	17.0
I	0.200	1.89	30 μA	100 μA	70 μA	0.53	17.0

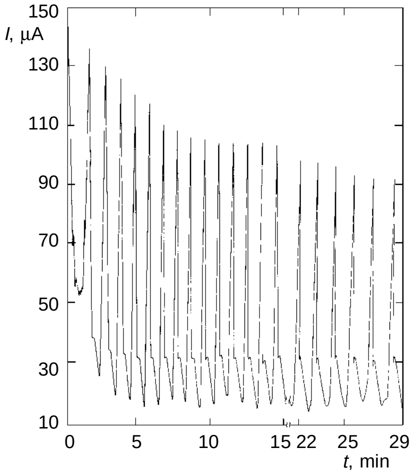

FIG. 3
Current oscillatory behaviour of malic acid–bromate system under the application of 200 mV of external EMF. Concentration conditions: 0.05 M $KBrO_3$, 1.0 M H_2SO_4, 0.05 M malic acid, 0.005 M $MnSO_4$

$$S + Br_2 \rightleftharpoons Br{\cdot}S + Br^- + H^+ \qquad (5)$$

$$S + M^{(n+1)+} \rightleftharpoons M^{n+} + H^+ + P\ , \qquad (6)$$

where S is substrate (malic, citric or malonic acid), Br·S is brominated substrate and P is product.

Citric acid and malic acid do not undergo direct bromination. Citric acid is oxidized to acetone dicarboxylic acid, which can undergo facile bromination with its two active methylene groups leading to the formation of pentabromoacetone as the final product. Malic acid undergoes oxidation to oxalacetic acid. Its single active methylene group is involved in the bromination step[11]. Thus, in the citric acid system there is an enhanced consumption of bromine leading to decrease in the potential range of oscillations. An application of external EMF has very similar effect to that for malic acid system. The prominence of the shoulder characteristic for bromine in the current profile is also in consequence of higher reactivity of citric acid (Fig. 5) compared to malic acid.

Malonic Acid–Bromate System

In the malonic acid system the frequency of potential and current oscillations under the concentrations indicated in Table III is the same (1.5 min^{-1}). The potential range of oscillations 0.750–0.945 V *vs* SCE indicates mixed control by both the redox couples Mn(III)/Mn(II) and Br_2/Br^-. The presence of active methylene group in malonic acid facilitated direct bromination unlike in case of malic acid and citric acid. The behaviour of the system under the influence of external EMF is similar to that with the other two

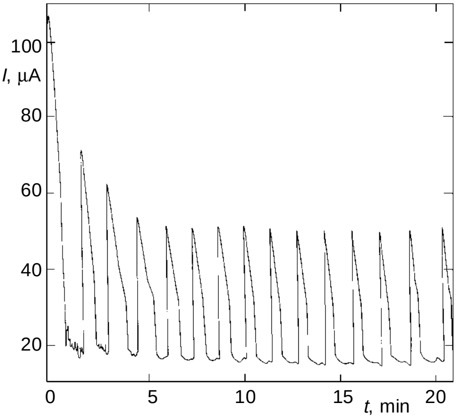

FIG. 4
Current oscillatory behaviour of malic acid–bromate system with 0.005 M TSPP under the application of 100 mV of external EMF

substrates. Thus, the conclusions already drawn on the nature of the processes are confirmed by the behaviour of the system with malonic acid as the substrate.

CONCLUSION

The study of Belousov–Zhabotinsky system under the influence of external EMF with Mn(II) as the catalyst and three different substrates provides valuable information regarding the course of the reactions. The application of external EMF shifts the potential range of the oscillations to the higher potential range by the extent of magnitude of the applied EMF. However, the amplitude of current oscillations increases with the increase in the magnitude of applied EMF. The behaviour of the system can be understood in terms of individual steps involved in the mechanism of the overall reaction.

TABLE III
Current (*I*) and potential (*E*) oscillatory behaviour of malonic acid; system: 0.05 M $KBrO_3$, 1.0 M H_2SO_4, 0.05 M malonic acid, 0.005 M $MnSO_4$; temperature 30 ± 0.1 °C

Measurement	External EMF V	Frequency of oscillations min^{-1}	Base value	Peak value	Amplitude	Wave number	Duration of oscillations min
E	0	1.49	0.750 V	0.945 V	0.195 V	0.67	40
E	0.100	1.56	0.850 V	1.050 V	0.200 V	0.64	45
I	0.100	1.56	0 μA	50 μA	50 μA	0.64	45
E	0.200	1.69	0.950 V	1.150 V	0.200 V	0.59	40
I	0.200	1.69	25 μA	80 μA	55 μA	0.59	40

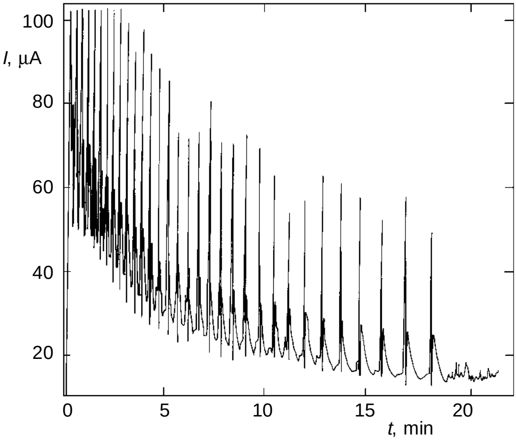

FIG. 5
Current oscillatory behaviour of citric acid–bromate system under the application of 200 mV of external EMF. Concentration conditions: 0.05 M $KBrO_3$, 1.0 M H_2SO_4, 0.05 M citric acid, 0.005 M $MnSO_4$

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