Mass-coupled CSTRs – cooperative dynamics in complex pH-oscillatory reactions

Lenka Schreiberová, Oldřich Pešek and Igor Schreiber

Institute of Chemical Technology Prague, Department of Chemical Engineering and Center for Nonlinear Dynamics of Chemical and Biological Systems, Technická 5,166 28 Praha 6, Czech Republic

Abstract

We present results of the experiments with two reaction cells coupled by diffusion-like mass transfer. The hydrogen peroxide-thiosulfate reaction catalyzed by Cu^{2+} in the solution of H_2SO_4 (HPTCu) was employed. We studied effects of the flow rate and intensity of coupling on autonomous dynamics of the system.

Introduction

Reaction between hydrogen peroxide and thiosulfate catalyzed by Cu^{2+} ions (HPTCu) in an isothermal stirred flow-through reactor is an autocatalytic chemical oscillator with large amplitude pH variations. In these pH–regulated reactions the concentration of hydrogen ions plays a critical kinetic governing role in the dynamical behaviour of system [1]. The oxidation–reduction reaction between H_2O_2 and $S_2O_3^{2-}$ in the presence of catalytic amount of Cu^{2+} has been shown to exhibit a rich variety of dynamical behavior if it is carried out in a continuos-flow stirred tank reactor (CSTR)[2,3].

Experimental setup

Experiments were carried out in a cascade of two reaction cells made of plexiglass covered on top by a teflon cap and coupled via an opening for mass transfer. A porous teflon grid was placed in the opening between both reaction cells so as to minimize convection flow caused by stirring. Each cell of volume 19 ml was stirred with a magnetic stirrer. Feed solutions were delivered with the use of a peristaltic pump (Ismatech). The solutions were prepared daily from standard commercially available chemicals. Required temperature of 25°C was maintained via a thermostat (Haake). The cells have a metal bottom to ensure rapid heat exchange with the coolant. Temperature and pH in the reactors were monitored during experiments by means of platinum thermocouples (Pt100) and glass combined pH-electrodes, respectively. The signals were amplified, digitized, processed and stored in a computer. The whole experiment, variation of the flow rate and data processing was controlled by a special program designed in the LabVIEW programming environment. Feed concentrations were chosen as follows: $c(H_2O_2)=0.1$ mol/l, $c(S_2O_3^{2-})=0.008$ mol/L, $c(Cu^{2+})=2.5\cdot10^{-5}$ mol/L, $c(H_2SO_4)=0.001$ mol/L.

At the start of an experiment the selected coupling strength and initial flow rate were set. After an initial transient period the measurement started. The control program set a flow rate delivered by the peristaltic pump feeding the first reactor and successively varied the flow after a chosen time interval. The flow was varied stepwise from minimal to maximal value and then backward again so as to detect any possible hysteresis. The period of changes had to be long enough so that a sustained dynamical regime is obtained. The flow rate of the peristaltic pump feeding the second reactor is kept constant at the value, where single reactor would oscillate.

Results

Variation of the system's dynamics as the constraints are varied was examined by Orbán and Epstein [2]. They found that pH of the system corresponds to: steady state I (SSI) – pH

~ 7-9, steady state II (SSII) – pH ~ 5, steady state III (SSIII) – pH ~ 3,5 and oscillations. In addition, the steady states may coexist and the system will operate at one of the alternative attractors depending on its history. In our earlier work we found that there are also parameter regions, where the system is excitable to pulsed addition of selected chemical species [4].

In the present experiments in coupled cells we study synchronization between two oscillators. An example of a measured time series is shown in Fig. 1, where the change of dynamical behavior is monitored in time as the flow rate k_0 is stepwise varied. For further analysis of the dynamics the recorded time series are used to construct one-parameter diagrams where the dependence of pH in both reactors on the flow rate (reciprocal residence time) in the first reactor k_{01} is represented (Figs. 2-3).
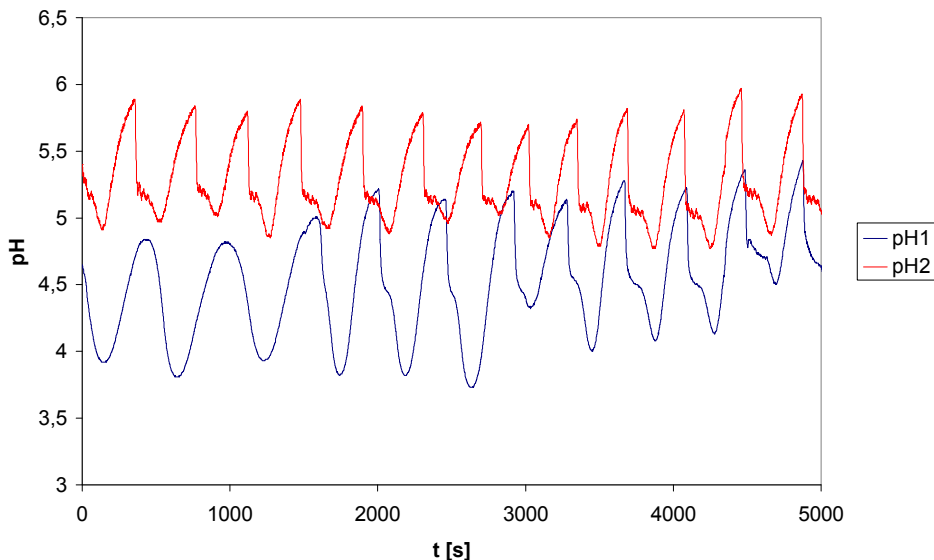
Fig. 1 Measured time series, $[H_2O_2]_{01} = [H_2O_2]_{02} = 0.1$ mol/L; $[S_2O_3^{2-}]_{01} = [S_2O_3^{2-}]_{01} = 0.008$ mol/L; $[H_2SO_4]_{01} = [H_2SO_4]_{02} = 0.001$ mol/L; $[Cu^{2+}]_{01} = [Cu^{2+}]_{01} = 2.5 \cdot 10^{-5}$ mol/L; $k_{01} = 0.0005, 0.001, 0.0015, 0.002$ s^{-1}(varied every 1500 s); $k_{02} = 0.003$ s^{-1}; K = 0.00015 s^{-1}
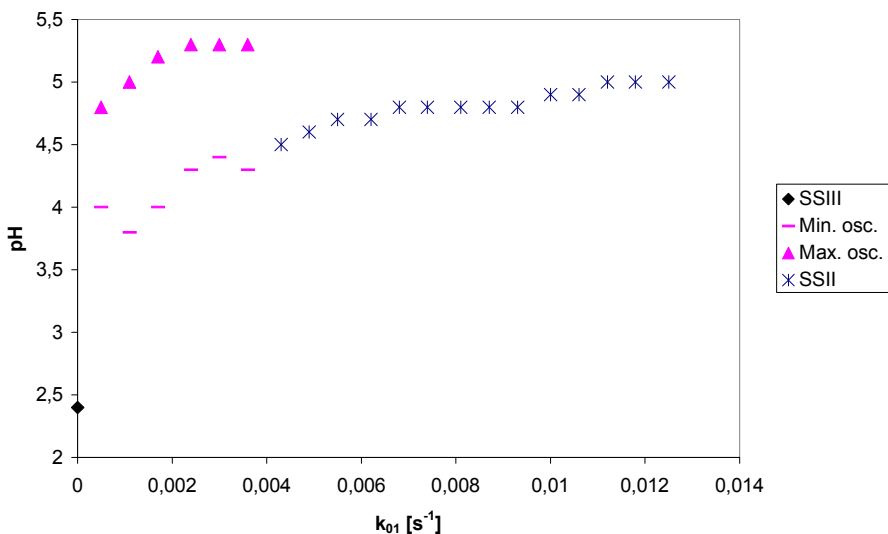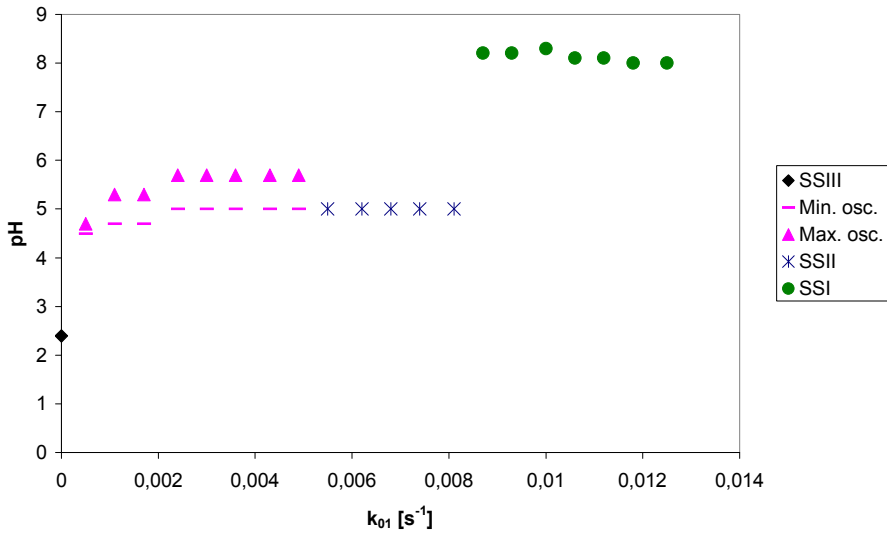
Fig. 2 One-parameter diagram for the first reactor with increased flow rate, $[H_2O_2]_{01} = [H_2O_2]_{02} = 0.1$ mol/L; $[S_2O_3^{2-}]_{01} = [S_2O_3^{2-}]_{01} = 0.008$ mol/L; $[H_2SO_4]_{01} = [H_2SO_4]_{02} = 0.001$ mol/L; $[Cu^{2+}]_{01} = [Cu^{2+}]_{01} = 2.5 \cdot 10^{-5}$ mol/L; $k_{02} = 0.003$ s^{-1}; K = 0.00015 s^{-1}

Fig. 3 One-parameter diagram for the first reactor with decreased flow rate, $[H_2O_2]_{01} = [H_2O_2]_{02} = 0.1$ mol/L; $[S_2O_3^{2-}]_{01} = [S_2O_3^{2-}]_{01} = 0.008$ mol/L; $[H_2SO_4]_{01} = [H_2SO_4]_{02} = 0.001$ mol/L; $[Cu^{2+}]_{01} = [Cu^{2+}]_{01} = 2.5 \cdot 10^{-5}$ mol/L; $k_{02} = 0.003$ s^{-1}; $K = 0.00015$ s^{-1}

The system can be found in a combination of the four aforementioned dynamical regimes, the state of system depends on direction of changes of flow rate thus its history and the reactors influence each other.

Series of experiments for various coupling strength are summarized in bifurcation diagrams, which are plotted in the parameter plane of the flow rate (reciprocal residence time) k_0 and mass transfer coefficient K (Figs. 4-5). The figures show, that the coupling caused a disappearance of bistability between SS II and SS I in the first reactor and an extinction of oscillations in the second reactor, where oscillations are replaced by SS III.
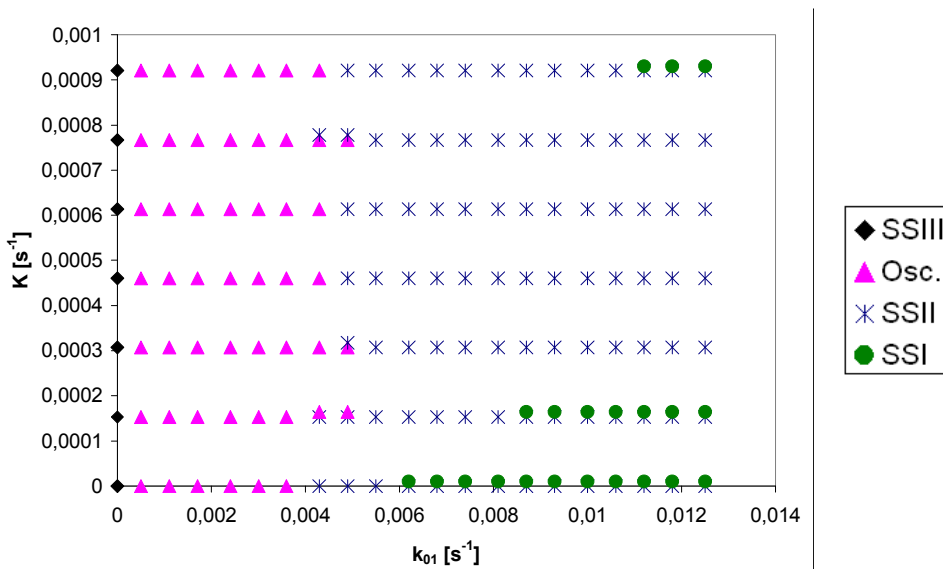

Fig. 4 Bifurcation diagram for the first reactor, $[H_2O_2]_{01} = [H_2O_2]_{02} = 0.1$ mol/L; $[S_2O_3^{2-}]_{01} = [S_2O_3^{2-}]_{01} = 0.008$ mol/L; $[H_2SO_4]_{01} = [H_2SO_4]_{02} = 0.001$ mol/L; $[Cu^{2+}]_{01} = [Cu^{2+}]_{01} = 2.5 \cdot 10^{-5}$ mol/L; $k_{02} = 0.003$ s^{-1}
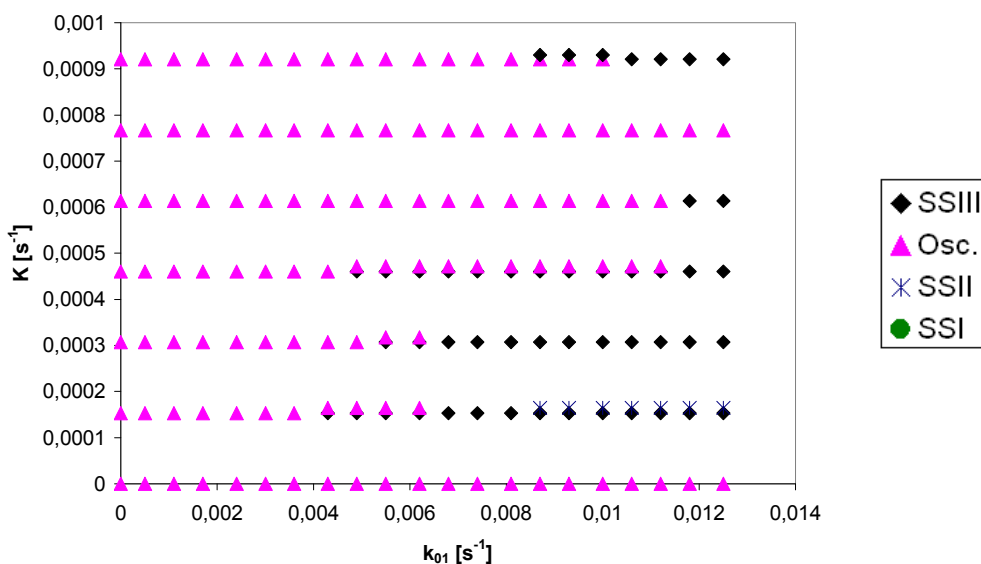
Fig. 5 Bifurcation diagram for the second reactor, $[H_2O_2]_{01} = [H_2O_2]_{02} = 0.1$ mol/L; $[S_2O_3^{2-}]_{01} = [S_2O_3^{2-}]_{01} = 0.008$ mol/L; $[H_2SO_4]_{01} = [H_2SO_4]_{02} = 0.001$ mol/L; $[Cu^{2+}]_{01} = [Cu^{2+}]_{01} = 2.5 \cdot 10^{-5}$ mol/L; $k_{02} = 0.003$ s^{-1}

Discussion and conclusions

Due to its complex mechanism, the H_2O_2-$S_2O_3^{2-}$-H_2SO_4-Cu^{2+} system displays a rich variety of dynamical regimes including multiple steady states and periodic oscillations in a single CSTR. We found that by coupling two nonidentical reactors, dynamical behavior becomes more complex than each of the two reactors separately. We measured time series of pH in a cascade of two mutually connected reaction cells with various intensity of mass transfer and flow rate in the first reactor. Data were processed and represented in terms of evolution (one-parameter) diagrams and then bifurcation diagrams were constructed in the plane k_0-K. These diagrams display parameter regions corresponding to various dynamical regimes. We focused mainly on the effects of coupling on the dynamical behavior. The studied system serves as a representative model for more complex biochemical and biological systems that are frequently pH-sensitive and can be represented as coupled subsystems.

References

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