Electronic Supplementary Material (ESI) for ChemComm.

Supporting Informations

Generation of spatiotemporal calcium patterns through coupling a pH-oscillator to a complexation equilibrium

István Molnár, Krisztina Kurin-Csörgei,
Miklós Orbán, and István Szalai
Institute of Chemistry, Eötvös Loránd University,
Budapest, Hungary

Experimental section

Open spatial reactors are designed to maintain a chemical reaction-diffusion system at controlled distance from thermodynamic equilibrium. In the version used here (Fig. 1) a thin sheet of gel is in contact by one face with the contents of a continuous-strirred-tank-reactor (CSTR). Opposite to the feed face the gel is pressed against an impermeable and transparent wall. Chemicals react both in the CSTR and in the gel. Only the chemical feed concentrations $[\mathrm{X}_i]_0$ of the CSTR are experimentally controlled. Here, we used disc-shape gels made of 2 w/w% agarose (Fluka 05077). It has an effective contact diameter of 25 mm and thickness of 0.75 mm in the x-direction. The residence time in the CSTR was fixed to 500 s, while the temperature was 30°C. The feed solutions of the major chemicals are stored in four separated tanks but enter premixed into the CSTR. Reactants are distributed in the feed tanks as follows:
Tank 1: $NaBrO_3$ (Sigma-Aldrich)+ sodium bromocresol green (Sigma-Aldrich) or arseneazo III (Fluka) indicator Tank 2: Na_2SO_3 (Sigma-Aldrich) + sodium bromocresol green (Sigma-Aldrich) or arseneazo III (Aldrich). Tank 3: $K_4Fe(CN)_6 \cdot 3\,H_2O$ (Sigma-Aldrich). Tank 4: Sulphuric acid diluted from 1.0 mol/L standard solution (Sigma-Aldrich). All solutions were prepared with deionized water and chemicals were used without further purification. The following input feed concentrations were kept fixed in all the experiments: $[NaBrO_3]_0 = 65\,\mathrm{mM}$, $[Na_2SO_3]_0 = 80\,\mathrm{mM}$, $[\text{sodium bromocresol green}]_0 = 0.2\,\mathrm{mM}$ or $[\text{arseneazo III}]_0 = 0.25\,\mathrm{mM}$. To produce calcium patterns calcium-disodium-EDTA salt was added to Tank 1 and its input feed concentration was $[CaNa_2EDTA]_0 = 2.0\,\mathrm{mM}$. To visualise the pH patterns bromocresol green indicator was selected and the reactor was illuminated through a narrow band-pass filter centred at $\lambda = 590 \pm 5$nm. The calcium patterns were visualised by using arseneazo III indicator. The spectra of arseneazo III and its calcium complex is peresented in Figure 4. In these experimenst the reactor was illuminated through a narrow band-pass filter centred at $\lambda = 650 \pm 5$nm, where mainly the absorbance of the calcium-arseneazo III complex is followed. The pictures were

taken by using a AVT Stingray F-033B (656 × 492, 14 bit) camera and recorded by the Streampix (Norpix) software. The image processing are made by using ImageJ [http://rsb.info.nih.gov/ij/]. The state of the CSTR composition was monitored by the recording the potential of a pH electrode.

Simulations section

The chemical equations of a general two substrate pH oscillator model coupled to a complexation equilibrium are as follows:

$$\mathrm{A^- + H^+ \rightleftharpoons HA} \tag{R1}$$

$$\mathrm{B + HA \xrightarrow{H^+} H^+ + P} \tag{R2}$$

$$\mathrm{C + H^+ \longrightarrow Q} \tag{R3}$$

$$\mathrm{S^- + M^+ \rightleftharpoons MS} \tag{R4}$$

$$\mathrm{S^- + H^+ \rightleftharpoons HS} \tag{R5}$$

with the reaction rates of:

$$v_1 = k_1[\mathrm{A^-}][\mathrm{H^+}] - k_{1b}[\mathrm{HA}] \tag{1}$$

$$v_2 = (k_2 + k_2'[\mathrm{H^+}])[\mathrm{HA}][\mathrm{B}] \tag{2}$$

$$v_3 = k_3[\mathrm{C}][\mathrm{H^+}] \tag{3}$$

$$v_4 = k_4[\mathrm{S^-}][\mathrm{M^+}] - k_{4b}[\mathrm{MS}] \tag{4}$$

$$v_5 = k_5[\mathrm{S^-}][\mathrm{H^+}] - k_{5b}[\mathrm{HS}] \tag{5}$$

where, k_2' is the rate constant of the autocatalytic pathway.

The corresponding set of differential equations for the CSTR content can be written as:

$$\tag{6}$$

$$d[\mathrm{A^-}]_{\mathrm{cstr}}/dt = -v_1 + k_0\left([\mathrm{A}]_0 - [\mathrm{A^-}]_{\mathrm{cstr}}\right) \tag{7}$$

$$d[\mathrm{H^+}]_{\mathrm{cstr}}/dt = -v_1 + v_2 - v_3 - v_5 + k_0\left([\mathrm{H}]_0 - [\mathrm{H^+}]_{\mathrm{cstr}}\right) \tag{8}$$

$$d[\mathrm{HA}]_{\mathrm{cstr}}/dt = v_1 - v_2 - k_0[\mathrm{A^-}]_{\mathrm{cstr}} \tag{9}$$

$$d[\mathrm{B}]_{\mathrm{cstr}}/dt = -v_2 + k_0\left([\mathrm{B}]_0 - [\mathrm{B}]_{\mathrm{cstr}}\right) \tag{10}$$

$$d[\mathrm{C}]_{\mathrm{cstr}}/dt = -v_3 + k_0\left([\mathrm{C}]_0 - [\mathrm{C}]_{\mathrm{cstr}}\right) \tag{11}$$

$$d[\mathrm{S^-}]_{\mathrm{cstr}}/dt = -v_4 - v_5 + k_0\left([\mathrm{S^-}]_0 - [\mathrm{S^-}]_{\mathrm{cstr}}\right) \tag{12}$$

$$d[\mathrm{HS}]_{\mathrm{cstr}}/dt = v_5 - k_0[\mathrm{HS}]_{\mathrm{cstr}} \tag{13}$$

$$d[\mathrm{M^+}]_{\mathrm{cstr}}/dt = -v_4 + k_0\left([\mathrm{M^+}]_0 - [\mathrm{M^+}]_{\mathrm{cstr}}\right) \tag{14}$$

$$d[\mathrm{MS}]_{\mathrm{cstr}}/dt = v_4 - k_0[\mathrm{MS}]_{\mathrm{cstr}} \tag{15}$$

where, the values of v_i are functions of the concentrations of the species in the CSTR.

The reaction-diffusion equations describing the 1D dynamics along the axial direction (x) of the gel content are written as:

$$\partial_t[\mathrm{A}^-] = -v_1 + D\partial_x^2[\mathrm{A}^-] \tag{16}$$

$$\partial_t[\mathrm{H}^+] = -v_1 + v_2 - v_3 - v_5 + D_{H^+}\partial_x^2[\mathrm{H}^+] \tag{17}$$

$$\partial_t[\mathrm{HA}] = v_1 - v_2 + D\partial_x^2[\mathrm{HA}] \tag{18}$$

$$\partial_t[\mathrm{B}] = -v_2 + D\partial_x^2[\mathrm{B}] \tag{19}$$

$$\partial_t[\mathrm{C}] = -v_3 + D\partial_x^2[\mathrm{C}] \tag{20}$$

$$\partial_t[\mathrm{S}^-] = -v_4 - v_5 + D\partial_x^2[\mathrm{S}^-] \tag{21}$$

$$\partial_t[\mathrm{HS}] = v_5 + D\partial_x^2[\mathrm{HS}] \tag{22}$$

$$\partial_t[\mathrm{M}^+] = -v_4 + D\partial_x^2[\mathrm{M}^+] \tag{23}$$

$$\partial_t[\mathrm{MS}] = v_4 + D\partial_x^2[\mathrm{MS}] \tag{24}$$

where, the values of v_i are functions of the concentrations of the species in the gel.

Dirichlet boundary conditions applied at the gel/CSTR surface:

$$c_{(x=0)} = c_{\mathrm{cstr}} \,\forall\, \text{species} \tag{25}$$

and no flux boundary conditions applied at the gel/impermeable wall surfaces:

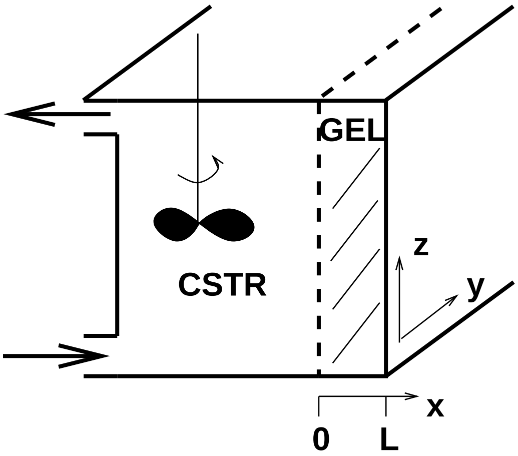
$$(\partial_x c)_{(x=L)} = 0 \,\forall\, \text{species} \tag{26}$$

The parameters of the model are:
k_1=10^{10} $\mathrm{M^{-1}s^{-1}}$
k_{1b}=10^3 $\mathrm{s^{-1}}$
k_2=10 $\mathrm{M^{-1}s^{-1}}$
k_2'=10^7 $\mathrm{M^{-2}s^{-1}}$
k_3=10 $\mathrm{M^{-1}s^{-1}}$
k_5=10^{10} $\mathrm{M^{-1}s^{-1}}$
k_{5b}=1 $\mathrm{s^{-1}}$
k_4=10^{10} $\mathrm{M^{-1}s^{-1}}$
k_{4b}=10^{-1} $\mathrm{s^{-1}}$
$[\mathrm{H}^+]_0$=0.14 mM
$[\mathrm{C}]_0$=0.1 mM
$[\mathrm{A}]_0$=10 mM
$[\mathrm{B}]_0$=15 mM,
$[\mathrm{S}]_0$=0.1 mM
$[\mathrm{M}]_0$=0.1 mM
D=10^{-5} $\mathrm{cm^2/s}$
D_{H^+}=9×10^{-5} $\mathrm{cm^2/s}$
k_0=2×10^{-3} $\mathrm{s^{-1}}$

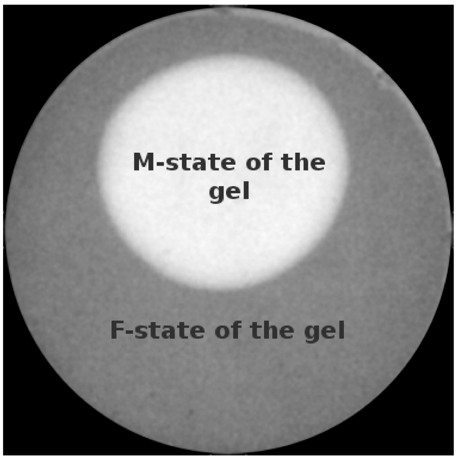
The numerical simulations were performed by using a ”method of line“ technique and a second order finite difference scheme and CVODE integrator. [Hindmarsh, A. C.; Brown, P. N.; Grant, K. E.; Lee, S. L.; Serban, R.; Shumaker, D. E.; Woodward, C. S. *SUNDIALS, Suite of Nonlinear and Differential/Algebraic Equation Solvers.* ACM Trans. Math. Software 2005, **31**, 363-396.]

Supplementary movies are available:

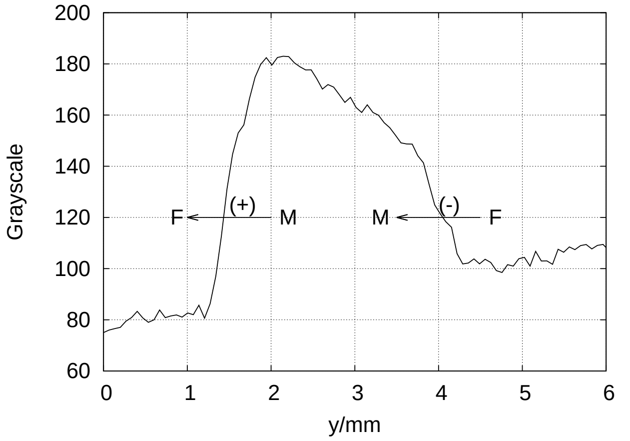
- bsf-ph-osc1.mov: spatiotemporal pH oscillations in the bromate-sulfite-ferrocyanide reaction at $[H_2SO_4]_0 = 7.4\,\mathrm{mM}$
- bsf-ph-osc2.mov: spatiotemporal pH oscillations in the bromate-sulfite-ferrocyanide reaction at $[H_2SO_4]_0 = 7.5\,\mathrm{mM}$
- bsf-ph-osc3.mov: spatiotemporal pH oscillations in the bromate-sulfite-ferrocyanide reaction at $[H_2SO_4]_0 = 7.6\,\mathrm{mM}$
- bsf-caedta-osc1.mov: spatiotemporal calcium oscillations in the bromate-sulfite-ferrocyanide-CaEDTA reaction at $[H_2SO_4]_0 = 6.8\,\mathrm{mM}$
- bsf-caedta-osc2.mov: spatiotemporal calcium patterns in the bromate-sulfite-ferrocyanide-CaEDTA reaction at $[H_2SO_4]_0 = 6.9\,\mathrm{mM}$
- bsf-caedta-pattern.mov: spatiotemporal calcium patterns in the bromate-sulfite-ferrocyanide-CaEDTA reaction at $[H_2SO_4]_0 = 7.0\,\mathrm{mM}$



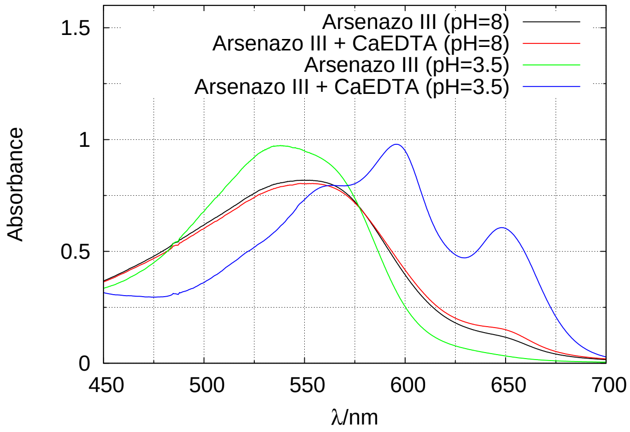
Supplementary Figure 1: Sketch of an OSFR.



Supplementary Figure 2: Illustration of the F- and M-states of the gel in the bromate-sulfite reaction. At the actual conditions the M-state domain increases in the expense of the F-state.



Supplementary Figure 3: Grayscale profiles of the (+) and (−) fronts in the bromate-sulfite-ferrocyanide reaction.



Supplementary Figure 4: Spectra of arseneazo III and its calcium complex at two different pH values.