A simple hydrogel device with flow-through channels to maintain dissipative non-equilibrium phenomena

supplementary information

Brigitta Dúzs and István Szalai*

Institute of Chemistry, Eötvös University, Budapest, Hungary

E-mail: szalai.istvan@chem.elte.hu
Supplementary Figures

Supplementary Figure 1: Photos of plexi molds used in four different reactor constructions. The devices are different in the diameter of the channels ($d$), in the distance between the channels ($w$) and the number of the channels ($n$). Parameters: (a) $d=4.5\text{ mm}$, $w=2.5\text{ mm}$, $n=2$; (b) $d=4.5\text{ mm}$, $w=10\text{ mm}$, $n=2$; (c) $d=1.3\text{ mm}$, $w=2.5\text{ mm}$, $n=2$; (d) $d=4.5\text{ mm}$, $w=2.5\text{ mm}$, $n=3$. 
Supplementary Figure 2: Experimental results with the BSF pH oscillator in the miniaturized reactor by using agarose gel (a) and in the normal sized reactor by using polyacrylamide gel (b-d). Space-time plots (a-c) and a snapshot of the stabilized pattern (d). Experimental conditions: (a) $[\text{H}_2\text{SO}_4]_B=7\text{ mM}$, (b) $[\text{H}_2\text{SO}_4]_B=6\text{ mM}$, (c-d) $[\text{H}_2\text{SO}_4]_B=10\text{ mM}$; $[\text{BrO}_3^-]_A=200\text{ mM}$, $[\text{SO}_3^{2-}]_{A,B}=80\text{ mM}$, $[\text{Fe(CN)}_6^{4-}]_{A,B}=20\text{ mM}$, $[\text{BCG}]_{A,B}=0.1\text{ mM}$, $w=2.5\text{ mm}$, $T=35^\circ\text{C}$.

**Supplementary Methods**

**Derivation of the numerical model**

The simulations were made by the dimensionless equations derived from the Rábai model of the pH oscillators (R1)-(R3).\(^1\)

\[
\begin{align*}
A^- + H^+ & \rightleftharpoons HA \quad \text{(R1)} \\
\text{HA} + B & \xrightleftharpoons[H^+] \text{H}^+ + P \quad \text{(R2)} \\
C + B + H^+ & \rightarrow Q \quad \text{(R3)}
\end{align*}
\]
The corresponding rate equations are the following:

\[ v_1 = k_1[A^-][H^+] - k_{-1}[HA] \]  
\[ v_2 = (k_2[H^+] + k'_2)[HA][B] \]  
\[ v_3 = k_3[B][C][H^+] \]  

The dynamics of the gel content is governed by the following set of equations:

\[ \partial_t[A^-] = -k_1[A^-][H^+] + k_{-1}[HA] + D_{A^-}\Delta[A^-] \]  
\[ \partial_t[HA] = k_1[A^-][H^+] - k_{-1}[HA] - (k_2[H^+] + k'_2)[HA][B] + D_{HA}\Delta[HA] \]  
\[ \partial_t[H^+] = -k_1[A^-][H^+] + k_{-1}[HA] + (k_2[H^+] + k'_2)[HA][B] - k_3[B][C][H^+] \]  
\[ \quad + D_{H^+}\Delta[H^+] \]  
\[ \partial_t[B] = -(k_2[H^+] + k'_2)[HA][B] - k_3[B][C][H^+] + D_B\Delta[B] \]  
\[ \partial_t[C] = -k_3[B][C][H^+] + D_C\Delta[C] \]

Here \([\ ]\) denotes the space and time dependent concentration in the gel.

Dirichlet boundary conditions were used at the gel/channel surfaces, and no flux boundary conditions were used at the outer surfaces of the gel.

Supplementary Figure 3: The sketch of the applied mesh with boundary conditions

The dimensionless variables are defined as \( a = [A^-]/[A]_{tot}, \ a_h = [HA]/[A]_{tot}, \ h = [H^+]/[A]_{tot}, \ b = [B]/[A]_{tot}, \ c = [C]/[A]_{tot}, \) where \([A]_{tot} = [A^-] + [HA].\)
The equations for the content of the gel can be written as:

\[
\begin{align*}
\partial_t a &= -\kappa_1 a h + \kappa_{-1} a h + \Delta a \\
\partial_t a_h &= \kappa_1 a h - \kappa_{-1} a h - (\kappa_2 h + \kappa'_2) a_h b + \Delta a_h \\
\partial_t h &= -\kappa_1 a h + \kappa_{-1} a h + (\kappa_2 h + \kappa'_2) a_h b - \kappa_3 b c h + 4\Delta h \\
\partial_t b &= -(\kappa_2 h + \kappa'_2) a_h b - \kappa_3 b c h + \Delta b \\
\partial_t c &= -\kappa_3 b c h + \Delta c
\end{align*}
\]

The diffusion coefficients are set to be equal for all species except for the hydrogen ions, which diffuses 4 times faster than the other species.\(^2\)

The parameters are defined as: \(\kappa_1 = k_1[A]_{\text{tot}}/k_0\), \(\kappa_{-1} = k_{-1}/k_0\), \(\kappa_2 = k_2[A]_{\text{tot}}^2/k_0\), \(\kappa'_2 = k'_2[A]_{\text{tot}}/k_0\), \(\kappa_3 = k_3[A]_{\text{tot}}/k_0\). Here, \(k_0 = 2 \times 10^{-3}\text{s}^{-1}\) is a reciprocal residence time in the channels. The value of \(\kappa_1\), \(\kappa_{-1}\), \(\kappa_2\), \(\kappa'_2\), \(\kappa_3\) are set to \(5 \times 10^{10}\), \(5 \times 10^5\), \(5 \times 10^5\), \(5 \times 10^1\), \(5 \times 10^3\), respectively. Parameters used in the simulations: \(b = 1.5\), \(a = 1.0\), \(c = 1.0\) in the Left channel and \(a = 1.0\), \(c = 1.0\) and variable value of \(h\) in the Right channel.

### Supplementary References

1. Rabai, G. Modeling and Designing of pH-Controlled Bistability, Oscillations, and Chaos in a Continuous-Flow Stirred Tank Reactor. *ACH - Models Chem.* 1998, 135, 381–392.

2. Schuszter, G.; Gehér-Herczegh, T.; Szűcs, Á.; Tóth, Á.; Horváth, D. Determination of the diffusion coefficient of hydrogen ion in hydrogels. *Phys. Chem. Chem. Phys.* 2017, 19, 12136–12143.