Peristaltic waves in a responsive gel sustained by a halogen-free non-oscillatory chemical reaction

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ABSTRACT

Formerly, we demonstrated in three chemical systems how the combination of the shrinking response of an appropriate responsive gel and a pH-switch type chemical reaction, which is not capable of oscillations by itself, can lead to self-oscillations in size and in pH in a piece of gel surrounded by a constant environment. We demonstrate that this can be realized at very mild chemical conditions: at ionic strength ~0.015 M, with acid generated in concentrations ~10 micromol/liter, and without halogen-containing oxidant. We discuss in detail how to adjust the gel-response to the chemical reaction for sustained motion. Travelling contraction wave trains along a long thin cylinder ($R_{sw} < 0.50$ mm) were sustained for more than 2 days. Considering the environmentally neutral reaction wastes, free from halogens or metal ions, biomaterials become attainable matrices in contrast to former chemomechanical oscillators which all operated under much harsher chemical conditions.

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1. Introduction

The first autonomous chemomechanical actuator, where a piece of gel was amazingly "self-oscillating", was driven by a pH-oscillatory chemical reaction, the hydrogen peroxide-sulphite-ferrocyanide (HPSF) reaction 20 years ago [1,2]. Interestingly, later no one returned to this chemical system. All other works used bromate as oxidizing agent [3–8] which usually means quite harsh chemical environment. Compared to them, the HPSF-driven gel system readily operated at very low concentrations (~2–6 mM) of the main reactants between pH 7.0 and 4.5. In these chemically driven periodic systems, with no exception, the "beating" lies in the chemistry, and the driven entities have to be able to synchronize with it [9]. In this sense, adaptation also means that the reversible process has to keep up with the chemical pulse clock. In living systems however, more and more evidence for the cross-dependence between biochemistry and mechanics (stress, elasticity, interfacial properties, transport) is recognized; such as e.g., in morphogenesis [10], heart functioning [11,12], or cytosol transport [13] where taken separately the biochemical and mechanical subsystems are not accountable for the behaviour. The new property emerges exclusively through the synergism [14,15] between chemistry and mechanics [16,17].

The concept that periodic deswelling–swelling cycles and chemical oscillations inside a chemoresponsive gel could be achieved even with no need for an oscillatory chemical reaction was proposed 12 years ago [18]. The energy source of these actuators lies in nonlinear chemical reactions (like autocatalytic reactions) that exhibit switch-like dynamic behaviour. The conversion is quasi-discontinuous: most of the time, the reaction is either in a quasi non-reacted state or in a practically completely reacted state; the latter occurs after an induction time (τ_{ind}) has passed since the mixing of the reactants. The other main condition for the operation (Fig. 1) is that the chemical environment of the responsive gel has to be kept at a given steady low extent of reaction composition (e.g., by the permanent feed of the reactants in a continuous-fed stirred tank reactor, CSTR, where τ_{CSTR} is the average residence time of the reactive solution in the CSTR), and let the reaction evolve only inside the gel. Under these conditions, the periodic behaviour arises from the mere synergy between a non-oscillatory chemical and a physical process. It is the changing characteristic time (τ_{diff}) of the transport process (diffusion) of the reactants and products between the environment and the core of a chemoresponsive gel that exerts a feedback on the chemistry. Swelling (increased τ_{diff}) can switch on the nonlinear chemical reaction in the gel while shrinking (shortened τ_{diff}) can turn it off. If the gel shrinks with a delay in response to one of the reaction products and the size-change is

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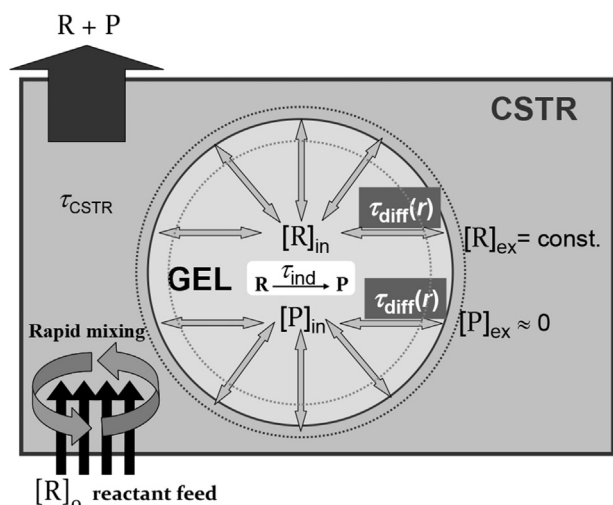 E-mail address: judit.horvath@chem.elte.hu.

Fig. 1. Schematic representation of the feed condition in a synergistic chemo-mechanical oscillator. The gel is suspended in a continuous-flow stirred tank reactor (CSTR), where a nonlinear (auto-activated) chemical reaction is kept at a low extent of reaction ("non-reacted") steady state ($\tau_{CSTR} < \tau_{ind}$). Reactants R and products P are diffusively exchanged between this chemical environment and the gel core with the characteristic time τ_{diff}. The reaction can spontaneously considerably evolve ("reacted" state) only inside the gel, provided that the reactants reside there longer than the induction time (τ_{ind}) of the nonlinear reaction. The extent of reaction (conversion) inside the gel depends sharply, with a hysteresis, on the gel radius (r) through τ_{diff}.

large enough, no steady-state is reached. Thus, chemomechanical oscillations arise (Fig. 2).

The first experimental demonstration of this operating principle was intended with the chlorite–tetrathionate (CT) reaction which was known to produce an extraordinary pH-drop (switch) of more than 7 units. It was presumed that nearly any pH-responsive gel would fit inside this pH-range and probably provide a suitable size-response. The advantage of the large amount of protons produced in this super-autocatalytic reaction turned out to be a drawback because it amplified any fluctuations (in size or in acid wave propagation rate) in an uncontrollable way, so very complicated non-periodic chemomechanical instabilities developed along a gel cylinder [19]. On the other hand, the extreme slowness of the initial stage of the CT reaction completely hampered the (re)starting of
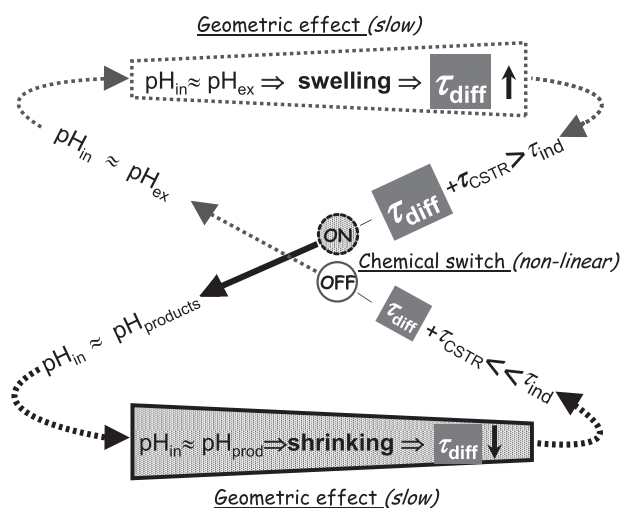

Fig. 2. The chart of the mechanism of a synergistic chemomechanical oscillator. It shows the pH changes in the gel (pH_{in}), the correlative changes in gel diameter, and the associated order relations of the three characteristic times (τ_{diff}, τ_{ind}, and τ_{CSTR}), which lead to the cyclic behaviour.

oscillations if no part of the gel was in the reacted state at one time [20]. The demonstration of the concept with the next reaction, the bromate-sulphite (BS) reaction, was of particular importance because a very realistic chemomechanical model had been developed based on the known kinetic mechanism of this reaction, and the simulations predicted genuine synergistic chemomechanical oscillations [21]. In the practice, this system was the first, based purely on the synergistic principle, which was capable of more than a dozen of periodic chemomechanical shrinking–swelling cycles and repeatedly lifting an object weighing more than ten-times the weight of the swollen gel [22]. Yet, the operation time was limited by a slow side-reaction between the BS reaction set and the gel network — as we suppose, by the bromination of the NIPA amide groups by hypobromite and other radicals present in the reaction front — thus resulting in the gradual loss of the shrinking capacity at a given temperature, and finally reaching a standstill after around 48 h.

The third pH-switch reaction used was a chemically less aggressive relative of the BS reaction, the iodate-sulphite (IS) reaction. This was the first synergistic system that generated constant-frequency large-amplitude chemomechanical oscillations that could be sustained for more than a week [23]! This prolonged and robust performance enabled to examine the temperature tolerance of operation and the effect of the molar ratio of the two reactants. This latter factor enabled to control whether the periodic lifting and lowering of the loading object was generated according to a square or a saw–tooth profile.

The key step in these advancements was the realization that the pH-switch range of the nonlinear chemical reaction was modified in the presence of weak acid functional groups, like the ones imperatively present in a pH-responsive gel. The pH-switch range reduced to 1/2–1/3, and in the case of the IS reaction also shifted. These aspects need to be experimentally estimated for each particular chemical reaction [24]. The exact tuning of the pH-response of the gel into the region of this effective pH-switch turned out to be the essential step in the design of these type of systems.

With the above results, Mikanohara et al. made attempts with the CT and BS reactions to generate peristaltic waves in tubular gels based merely on the synergistic concept [25,26]. In the tubular gels, the feed solution was cleverly let flow only through a 1.0 mm diameter axial channel through the gel, this way reactant solution consumption (and waste) was about only 1/10 of that of a CSTR experiment. Nonetheless, sustained peristaltic motion and material transport through tubular gels were actually realized only with a quite special oscillatory reaction [27,28].

In the present work, we aimed at constructing a synergistic chemomechanical oscillator based on the mildest member of the reaction family that the BS and IS reactions belong to: the hydrogen peroxide – sulphite (HPS) reaction. Another advantage of the HPS reaction when working with polyelectrolyte gels is the low ionic strength, as the oxidizing agent is non-ionic, so higher swelling degrees can be attained. As the BS and IS, the HPS reaction follows the general reaction scheme below [29].

$$A + H^+ \leftrightarrow HA$$

$$B + HA \rightarrow H^+ + P$$
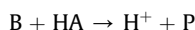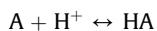
where A and B are the reactants, and P represents the products. A is sulphite and B is an oxidizing agent (bromate, iodate, or hydrogen peroxide). A and HA together act as a buffer system that maintains the solution pH close to neutral. B consumes this buffer system in a redox reaction. The loss of the buffer capacity results in a sudden pH drop due to the nonlinear relationship between them. To develop