Design and study of novel oscillatory chemical systems

PhD thesis

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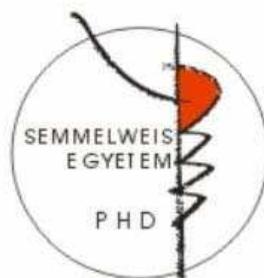
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I. Introduction

The *periodicity* is generally observed phenomenon in the living and unanimated environments. For example, repetition of days and nights, changes of the seasons, regular appearance of high and low tides, some steps in the glycolysis, periodic contraction of heart tissue, population dynamics in the animal world (pray and predator), periodical appearance of some infectious diseases, biological clock, formation of patterns on the animal coats and inside the rocks, etc. can serve as typical periodic phenomena. We encounter periodicity *in chemical systems* as well if special requirements are fulfilled. In such systems – depending on the way as the reaction is carried out – the concentration of the intermediates and even the reactants and products can undergo periodic changes during the course of the reaction. The oscillations in concentration may appear in time or space resulting in *oscillatory chemical reactions* or *chemical patterns*, respectively. The results established about the periodicity at molecular level may contribute to understand the similar but more complicated periodical phenomena emerging widely in nature.

II. Objectives

My doctoral work aimed at *producing novel oscillatory chemical reactions* by: (1) elaborating new design method; (2) applying known method; (3) finding systems of new composition. The additional tasks were to study and model the dynamical behavior of the new systems.

My objectives were:

(1) *Generation of batch pH-oscillators*:
All pH-oscillators known so far have worked under flow condition. Some of them are able to oscillate in semi-batch reactor, as well, these oscillations are strongly damped due to the constant increase of volume, the consumption of reactants and the dilution of the reaction mixture. Progresses in the applications of pH-oscillators ("molecular motors", "periodic drug delivery system", coupling pH-oscillators to biomolecules, e.g. to DNA or nanosystems, etc) made it necessary to develop hardly damped, high amplitude, long lasting closed pH-oscillatory systems.

(2) *Coupling metal ion − amino acid complex formation equilibrium to a pH-oscillator:*
Our research group has developed a method by which oscillations in the concentration of non-redox ions can be

induced. The method is based on linking a redox-oscillator to a complexation or precipitation equilibria. In the coupled system the concentration of the components participating in the equilibria is forced to oscillate with the frequency of the core oscillator. One of my tasks was to extend the number of coupled systems by using metal ions – amino acid complex formation instead of the previously applied inorganic chemical equilibria. In the new systems the concentration of the different amino acid complexes and the metal ion are expected to oscillate.

(3) *Design of new permanganate oscillators involving amino acids and studying the mechanism of the new system:*
So far only inorganic reductants were used in the manganese chemistry-based oscillators. The kinetics of the oxidation of some amino acids by permanganate was established and autocatalytic reaction path was reported in both acidic and neutral pHs. My aim was to produce a new group of manganese oscillators in which the substrates are amino acids.

III. Methods

The *CSTR* (continuous fed stirred tank reactor) *runs* were performed in V= 110 cm^3 and 25 cm^3 thermostated (T= 25 °C and 45 °C) reactor. The reactants were fed continuously by a peristaltic pump (Gilson Minipulse 2) through 4 silicone tubes. The excess of the reactor content was removed by another peristaltic pump that rotated in opposite direction. The reaction mixture was stirred by magnetic stirrer (Heidolph MR 3000). The changes in the pH in time were followed by a combined glass electrode (Radelkis OP-0823P). The redox potential in the reaction mixture was measured by Pt electrode (reference electrode Hg / Hg$_2$SO$_4$ / K$_2$SO$_4$). The electrodes were connected to pH-meter (Hanna pH 209). The data were recorded by a two-channel analog recorder (Kipp & Zonen BD 41) and with a personal computer using a NI 6010PCI A/D converter.

In the *semi-batch experiments*, the reactor was filled with the mixture of components in excess. The reagent consumed during one oscillatory cycle was introduced into the reaction vessel at slow flow rate by a peristaltic pump.

The setup used *in closed system* experiments was much simpler. After filling the reactor with the components of the oscillator no additional input from outside was introduced.

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Silica gel layers of different thickness containing sodium sulfite were prepared previously in the reaction vessel and supplied the sulfite by slow dissolution. The mixture of the other components was prethermostated, poured above the gel and the pH was measured in time. In order to avoid any damage of the gel the solution was stirred from above (IKA RW 20 Digital) with low rate (100-250 rpm) instead of using a magnetic stirrer.

In the experiments needed to accomplish Objectives (2) and (3) *spectrophotometric measurements* were carried out by using Milton Roy 3000 (λ= 300-800 nm, l= 1 cm quartz cuvette, T= 25-45 °C) and Agilent 8452 type (λ= 300-800 nm, l= 3.27 cm, T= 45 °C) diode array spectrophotometers.

The simulations were done with the program XPPAUT. The calculations of species distribution in the metal ion – amino acid complex equilibrium as a function of pH were performed with the MEDUSA software package.

IV. Results

The results achieved in my doctoral work are the followings:

(1) A method was elaborated which is able to convert CSTR pH-oscillators to closed ones. All known pH-oscillators function under flow condition, because one of the reagents is consumed during one oscillatory cycle. To maintain the oscillations this reagent should be continuously supplied. If we generate this reagent inside the reactor CSTR pH-oscillators can be converted to batch-like versions. Our method is based on supplying the reagent by its dissolution from gel layer prepared previously in the reactor. With the method four pH-oscillators, the $BrO_3^- - SO_3^{2-} - Mn^{2+}$, the $BrO_3^- - SO_3^{2-} - Fe(CN)_6^{4-}$, the $IO_3^- - SO_3^{2-} - Fe(CN)_6^{4-}$ and the $BrO_3^- - SO_3^{2-}$ CSTR pH-oscillators were transformed to operate under closed condition. In a batch system that consisted of a gel layer embedded with Na_2SO_3 and of a solution which contained the rest of the components of the above mentioned CSTR pH-oscillators hardly damped, large amplitude, long lasting pH-oscillations were recorded. Dissolution rate of the sulfite from the silica gel was measured. The pH-oscillations measured in

the BrO_3^- – SO_3^{2-} batch-like system was successfully simulated.

(2) Coupling pH-oscillators to metal ion – amino acid complex formation equilibrium was studied in order to extend the number of species that are capable of concentration oscillations. The species distribution as a function of pH was calculated and the light absorption spectra was recorded at different pHs at different initial molar ratios. Concentration oscillations of the Ni^{2+}, the $NiHis^+$ and the $Ni(His)_2$ species were measured in the coupled BrO_3^- – SO_3^{2-} – Ni^{2+} – histidine CSTR system. The dynamical behavior of the coupled system was simulated by model calculations.

Efforts were made to further extent the number of coupled system. In the BrO_3^- – SO_3^{2-} – Co^{2+} – histidine CSTR system high amplitude oscillations were observed in the absorbance at $\lambda = 418$ nm.

(3) A manganese-based oscillator which is new in composition was produced. In the $KMnO_4$ – glycine – $H_2PO_4^-$ CSTR system long period time (1 hour) oscillations in the redox potential and in the light absorption at $\lambda = 525$ nm and $\lambda = 418$ nm characteristic for MnO_4^- and $Mn(IV)$ions, respectively were measured. Model was suggested to explain the origin of

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oscillations and the dynamical behavior of the system was successfully simulated.

The permanganate oxidation of seven amino acids (glycine, alanine, threonine, valine, leucine, isoleucine, phenylalanine) has been reported to proceed in autocatalytic way. Oscillations were measured in the $KMnO_4$ – threonine – $H_2PO_4^-$ flow system as well.

In 1996 high frequency potential-oscillations have been found by a Chinese research group in the $KMnO_4$ – glicin – H_3PO_4 CSTR system. Despite our hard efforts we failed to reproduce their results. I proved by spectrophotometric measurements that the oscillations observed by the Chinese group are most probably artifact. Chemical oscillations found by us appear under significantly different conditions than those reported in 1996.

V. Conclusions

(1) *Generation of batch pH-oscillators*:

Our experimental results show that some CSTR pH-oscillators – using appropriate methods – can be converted to semi-batch and batch variants. The essential step of the method is the supplement of the reagent consumed during the oscillatory cycle. This reagent could be introduced by peristaltic pump in the semi-batch experiments or according to the proposed method, by its dissolution from another phase. The later mentioned arrangement represents a batch-like system. In this system sulfite ion was stored in gel-phase and pH-oscillations were measured in the mixture of other reagents. Beside the four successfully converted systems there are seven other pH-oscillators that contain sulfite ion as reductant. Presumably, many of them can be transformed to operate in semi-batch or batch condition with our method. In several proposed applications the batch-like pH-oscillators would be more convenient to use than the more complicated CSTR arrangement. Many other reagents can be embedded into gels, so this method may be suitable to convert not only CSTR pH-oscillators. Some promising preliminary experiments were carried out in the Cu(II)-catalysed oscillators (e.g. in the $H_2O_2 – S_2O_3^{2-} – Cu^{2+}$ system) to reach this goal.

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(2) *Coupling metal ion – amino acid complex formation equilibrium to a pH-oscillator:*

My experimental results proved that the pH-oscillators are capable of moving periodically such complicated equilibria as the stepwise complex formation reactions. In the coupled Ni^{2+} – histidine – BrO_3^- – SO_3^{2-} CSTR system the concentration of the Ni^{2+}, $NiHis^+$ and $Ni(His)_2$ oscillates. We may conclude that many other oscillators are able to alternate physical, chemical and biochemical equilibria periodically. We suppose that concentration oscillation of non-redox molecules or ions may occur similar way in the more complicated living organisms as in the simple chemical systems. Our results show that the behavior of complex systems can be predicted by model calculations using the data of the subsystems.

(3) *Design of new permanganate oscillators involving amino acids and studying the mechanism of the new system:*

I demonstrated that in oscillators based on manganese chemistry beside inorganic ions the more complicated organic compounds, such as amino acids could serve as reductant. Oscillations were observed in the permanganate oxidation of the simplest amino acid the glycine and the threonine, in the presence of $H_2PO_4^-$, at neutral pHs. The oscillatory ranges of the initial concentrations are narrower than observed in the

KMnO$_4$ – inorganic substrate – stabilizator systems. The range of parameters within the system behaves in oscillatory manner is significantly narrower compared to those in which inorganic substrate is involved. The permanganate oxidizes other amino acids such as valine, leucine, etc. in autocatalytic reactions. We assume that some of these amino acids or even some simple peptides can be used as substrates in manganese-chemistry based oscillators.

VI. Publications

1. **Poros E**, Horváth V, Kurin-Csörgei K, Epstein IR, Orbán M. (2011) Generation of pH-oscillations in Closed Chemical Systems: Method and Applications. J. Am. Chem. Soc., 133:7174-7179.

2. **Poros E**, Kurin-Csörgei K, Szalai I, Orbán M. (2013) Oscillations in the Permanganate Oxidation of Glycine in a Stirred Flow Reactor. J. Phys. Chem. A, 117(37):9023-9027.

3. **Poros E**, Kurin-Csörgei K, Horváth V, Szalai I, Orbán M. (2014) Periodic Changes in the Distribution of Species Observed in the Ni^{2+} – Histidine Equilibrium Coupled to the BrO_3^-–SO_3^{2-} pH-oscillator. J. Phys. Chem. A, 118(34):6749-6756.

4. **Poros E**, Kurin-Csörgei K, Szalai I, Rábai Gy, Orbán M. (2015) pH-oscillations in the bromate – sulfite reaction in semibatch and in gel-fed batch reactors. Chaos, 25(6): 064602. DOI:10.1063/1.4921176**.**