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**Hypoiodous acid measurement in the Briggs–Rauscher oscillating
reaction and coupling of pH oscillators**

Theses of Ph.D. dissertation

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1 Introduction, aim of the work

1.1 Research aims of studies on oscillating reactions

MOST of the studies devoted to oscillating reactions focus either on the mechanism or on the dynamics of the reaction.

Study of the reaction mechanism. The traditional chemical approach is to explore the mechanism. In this case it has a fundamental importance to use appropriate measurement techniques and to know which intermediates are taking part in the reaction. The Briggs-Rauscher oscillating reaction was monitored mostly with spectrophotometric and electrochemical techniques. Here we investigate which intermediates affect the potential of the most often used electrodes: the Ag/AgI and the Pt electrodes.

To create or understand a reaction mechanism it is important to identify its intermediates. Diiodine monoxide was suggested to have an essential role in the mechanism of the iodine oscillators. However, that intermediate has never been prepared previously; this is why we were motivated to prepare and identify that key intermediate.

Study of the dynamical behavior. Beside the investigation of the reaction mechanism the other general objective is the observation of the dynamical properties of the chemical oscillators. In this case the aim of the research is not the reaction mechanism but to find and identify new dynamical phenomena. That approach can be suitable for even more complex systems such as biological reaction networks or for living systems as well.

With coupled stirred tank reactors it is possible to create chemical dynamical systems which show new, exciting dynamical behavior. We demonstrate such a new dynamical behavior by coupling pH oscillators.

1.2 Studies related to the reaction mechanism of chemical dynamical systems

1.2.1 The Ag/AgI electrode as a HOI sensor

The presence and significance of hypoiodous acid. The study of iodine speciation in waters is of great significance for the proper daily iodine intake by humans and for atmospheric pollution. Iodine exists in seawater, rain, and municipal water mainly as iodide, iodate and organic compounds. Molecular iodine is also formed by oxidation of iodide or reduction of iodate, and the hydrolysis of iodine produces hypoiodous acid:



Hypoiodous acid is an important intermediate in the formation of iodine organic compounds and has a particularly important role in the exchange of iodine between seawaters and the atmosphere¹. HOI is also a component of the waste streams from nuclear reactors². On the other hand, hypoiodous acid is an intermediate in complex systems like the Bray–Liebhafsky³ (BL) and Briggs–Rauscher⁴ (BR) oscillating reactions. Kinetic studies such as modeling of all these systems would benefit greatly if we could understand which compounds are the generally used Ag/AgI and Pt electrodes sensitive to.

¹E. A. Pillar, M. I. Guzman, J. M. Rodriguez, *Environmental Science & Technology* **47**, PMID: 23987087, 10971–10979 (2013).

²J. R. Harrell, J. B. Lutz, J. L. Kelly, *Journal of Radioanalytical and Nuclear Chemistry* **127**, 13–20, ISSN: 1588-2780 (May 1988).

³W. C. Bray, *Journal of the American Chemical Society* **43**, 1262–1267 (1921).

⁴T. S. Briggs, W. C. Rauscher, *Journal of Chemical Education* **50**, 496 (1973).

The corrosion potential. Our research group has developed a new type of iodide selective electrode prepared by dipping silver wire into molten silver iodide. It was shown that the electrode (similarly to the traditional AgI pellet based iodide selective electrodes) responds not only to Ag^+ and I^- ions but is also sensitive to HOI above the so-called solubility limit potential (SLP), where

$$[\text{I}^-]_{\text{s}}^{\text{SLP}} = [\text{Ag}^+]_{\text{s}}^{\text{SLP}} = \sqrt{K_{\text{s}}}, \quad (1)$$

at the surface of the electrode where K_{s} is the solubility product of AgI.

The Nernstian potential response of the electrode to HOI was explained by the corrosion potential theory. In accordance with that theory, HOI reacts with the AgI coating of the electrode to generate Ag^+ ions in the corrosion reaction:



The electrode actually measures the steady-state concentration of Ag^+ ions at its surface, which is established in reaction and diffusion processes of the various components. The Nernstian potential response is due to a linear relationship between the Ag^+ ion concentration at the surface of the electrode and the HOI concentration in the bulk.

1.2.2 Objective I.

In the iodine oscillators above the SLP the iodine occurs in four oxidation state in a considerable amount: 0, 1, 3, 5. The effect of hypoiodous acid on the Ag/AgI electrode due to the corrosion process was investigated earlier⁵, and the effect of iodate was found negligible. However, HOIO (iodous acid) is present in a considerable amount as well in the iodine oscillators and its effect – according to the previous studies – can not be excluded. According to that our first aim was to investigate the corrosion potential of HOIO. Furthermore we investigated the corrosion potential when both HOIO and HOI were present in the solution. In these investigations we used sulphuric acid of 1 M – which is ~ 40 times more concentrated than the one unusually used in oscillating reactions – to strengthen the corrosion processes.

1.2.3 The Pt electrode in iodine oscillators

The potential-determining redox pair. The classical Briggs–Rauscher (BR) oscillation reaction is the reaction among H_2O_2 , malonic acid, and iodate in the presence of a Mn(II) catalyst in an acidic solution. Platinum and AgI electrodes have been used to follow oscillations. In most cases, however, these electrode potential vs time diagrams (potentiometric traces) are used only semiquantitatively. For example, the amplitude of the Pt potential oscillations is usually not taken into account when a BR oscillator is applied for analytical purposes. In that case, only the time period of the reaction or the number of oscillations is regarded.

Moreover, there is no general agreement concerning the potential-determining redox pair for a Pt electrode in the BR or in a BL reaction. Some authors assume that it is the $\text{HO}_2^\bullet/\text{H}_2\text{O}_2$ redox pair in a BR reaction⁶, whereas others suggest that the I_2/I^- redox couple plays a role of the potential-determining redox pair in the BL system.

1.2.4 Objective II.

The C 1 iodine hydrolysis equilibrium constant K_{H} :

$$K_{\text{H}} = \frac{[\text{I}^-][\text{H}^+][\text{HOI}]}{[\text{I}_2]}. \quad (2)$$

⁵N. Muntean, L. B. Thuy, K. Kály-Kullai, M. Wittmann, Z. Noszticzius, L. Onel, S. D. Furrow, *The Journal of Physical Chemistry A* **116**, PMID: 22554088, 6630–6642 (2012).

⁶K. Keresztúri, I. Szalai, *Zeitschrift für Physikalische Chemie* **220**, 1071 (2006).

Putting the iodide equilibrium concentration into the Nernst equation applied to the iodine/iodide redox couple we can see that – from a thermodynamic point of view – the platinum electrode is able to measure the hypiodous acid concentration too:

$$\begin{aligned}\varepsilon_{Pt} &= \varepsilon_{Pt}^0 + 59.16 \text{ mV} \lg \frac{[\text{H}^+]}{K_H} + 59.16 \text{ mV} \lg \frac{[\text{HOI}]}{\sqrt{[\text{I}_2]}} = \\ &= \varepsilon_{Pt}^{0*} + 59.16 \text{ mV} \lg \frac{[\text{HOI}]}{\sqrt{[\text{I}_2]}}.\end{aligned}\tag{3}$$

Similarly to this case we can use the Nernst equation to every iodine species. Our aim is to determine in a iodine oscillator, which oxyiodine species affect the potential of a platinum electrode. We have to take into account an oxyiodine species if it takes part in a fast surface reaction on the platinum electrode and gives a considerable exchange current.

1.3 One important intermediate: the diiodine monoxide

The I_2O has not been prepared, but it was proposed as an important intermediate of reactions in dilute acidic solutions. It is formed by the reaction $2 \text{HOI} \rightleftharpoons \text{I}_2\text{O} + \text{H}_2\text{O}$ but has never been observed directly because the equilibrium of this reaction is shifted to the left. The fundamental assumption in the mechanism of the Bray–Liebhafsky oscillations is that the reaction of HOI oxidation by hydrogen peroxide is second order with respect to [HOI]. This second order is explained if the $2 \text{HOI} \rightleftharpoons \text{I}_2\text{O} + \text{H}_2\text{O}$ preequilibrium is followed by the rate determining $\text{I}_2\text{O} + \text{H}_2\text{O}_2 \longrightarrow \text{HOI} + \text{HOIO}$ reaction. This mechanism was supported by a kinetic study of the iodine oxidation by hydrogen peroxide.

The disproportionation of HOI is also second order with respect of [HOI]⁷ but, despite the large number of kinetic studies, their mechanism is not well known. Our direct observation of the I_2O formation in concentrated sulfuric acid is an important argument supporting its role as an intermediate of these reactions in dilute sulfuric acid.

Iodine compounds coming from the marine boundary layer are transported to the upper troposphere and lower stratosphere (UT/LS) where they deplete extremely O_3 . I_2O had been mentioned as a possible intermediate of atmospheric reactions but does not appear in more recent models of the troposphere⁸. It could be produced by the reaction $\text{IO}^\bullet + \text{I}^\bullet + \text{M} \longrightarrow \text{IOI} + \text{M}$ or in the highly concentrated sulfuric acid droplets present in the UT/LS. Time-of-flight mass spectrometry experiments has shown that I_2O is one the iodine oxides generated by the reaction between I_2 and O_3 .

1.3.1 Objective III.

Despite the existence of I_2O was assumed just in models and it has not been prepared previously we can predict its properties based on two known species: the Cl_2O and the Br_2O . As the molar masses increase of the analogous halogen species the color becomes darker, furthermore the stability and the melting point decrease. Every known X_2O species are well soluble in carbon tetrachloride. According to that we can expect the I_2O to be a dark brown or black unstable species which is well soluble in carbon tetrachloride. Our aim was to synthesize I_2O in a high purity.

⁷S. Furrow, *The Journal of Physical Chemistry* **91**, 2129–2135 (1987).

⁸T. Sherwen, J. A. Schmidt, M. J. Evans, L. J. Carpenter, K. Großmann, S. D. Eastham, D. J. Jacob, B. Dix, T. K. Koenig, R. Sinreich, I. Ortega, R. Volkamer, A. Saiz-Lopez, C. Prados-Roman, A. S. Mahajan, C. Ordóñez, *Atmospheric Chemistry and Physics* **16**, 12239–12271 (2016).

1.4 Studies on dynamical properties of chemical dynamic systems

1.4.1 Coupling of pH oscillators

Control of master–slave systems. The ability to control and drive reversible chemical systems with autonomous stimuli, in particular, with pH oscillator, is of fundamental importance. These investigations contribute to the development of stimuli responsive materials, drug delivery applications, and novel self-organization/self-assembly techniques. In the past few years a new concept has been introduced to drive and control chemical equilibria (e.g., complexation, precipitation) by autonomous way using core oscillators.

The main characteristics of the master–slave coupling are that the master system (pH oscillator) drives the phenomenon and that the slave system (equilibrium reaction) does not interfere and change the main characteristics of the master system. Followed this basic idea several new slave systems have been introduced and coupled to pH oscillators.

The *feedback of the slave system* on the core oscillator has been rarely mentioned, the buffering effect of ethylenediaminetetraacetic acid (EDTA) on the characteristics the bromate–sulfite–ferrocyanide and Ca^{2+} coupled oscillating system was first indicated in the work of Kurin–Csörgei and her colleagues⁹. The authors found that at high EDTA concentration pH oscillations can be damped or even eliminated. Nabika and his co-workers reported that mercaptododecanoic acid-terminated gold nanoparticles can dramatically change the amplitude and time period of the driving oscillator (bromate–sulfite pH oscillator)¹⁰. In this study, the authors account that this effect is due to catalytic activity of gold nanoparticles. In another report, Dolnik and his colleagues showed that a chemical buffer can control the frequency and amplitude of the driving oscillator (bromate–sulfite pH oscillator)¹¹.

1.4.2 Objective IV.

Our aim is to present a new approach and provide a new terminology to study and analyze the coupling strategy between driving (master) and slave systems. We showed that by increasing the coupling species concentration, the feedback from the slave system to master system is more pronounced resulting in significant changes in the characteristics of the master system so we can get gradually a *peer-to-peer* coupling from the master–slave coupling.

From our investigations, we revealed that in one–volume homogeneous chemical reaction network pure master–slave coupling cannot be possible through a single coupling species, which is incorporated both in the kinetics of the master and slave subsystem. However, we would like to create the perfect master–slave coupling. To achieve that we separated spatially the master and the slave systems to exclude any feedback from the slave to the master system.

⁹K. Kurin-Csörgei, I. R. Epstein, M. Orbán, *The Journal of Physical Chemistry A* **110**, PMID: 16774201, 7588–7592 (2006).

¹⁰N. Hideki, I. Yusuke, O. Tetsuro, U. Kei, *Chemistry Letters* **41**, 1139–1141 (2012).

¹¹M. Dolnik, T. S. Gardner, I. R. Epstein, J. J. Collins, *Phys. Rev. Lett.* **82**, 1582–1585 (7 Feb. 1999).

2 Experimental section

2.1 Measurements with the Ag/AgI and the Pt electrode



VERY experiment was carried out in a double-walled thermostated glass beaker. The apparatus applied in the potentiometric and in the exchange current measurements with the Ag/AgI and the Pt electrodes can be seen in figure 1 (left). The multimeter (MM) and the source meter (SM) were controlled by a personal computer (PC). In the case of potentiometric experiments, the source meter and the Pt reference and auxiliary electrodes played no role, and the multimeter measured the potential periodically between the Pt working and the Ag/AgCl reference and also between the AgI and the Ag/AgCl electrodes. During exchange current measurements, the polarizing current was flowing between the working and the auxiliary electrodes (Pt working and Pt auxiliary, respectively), and the overpotential η was measured between the Pt working and the Pt reference electrodes.

The schematic drawing of the apparatus to measure mixed potentials can be seen in figure 1 (right). AgI(test), Pt(test), AgI(pert.), and Pt(pert.) indicate the wires leading from the multimeter, MM, to the test and the perturbing electrodes, respectively. Switches S1 and S2 could connect or disconnect the test and the perturbing electrodes.

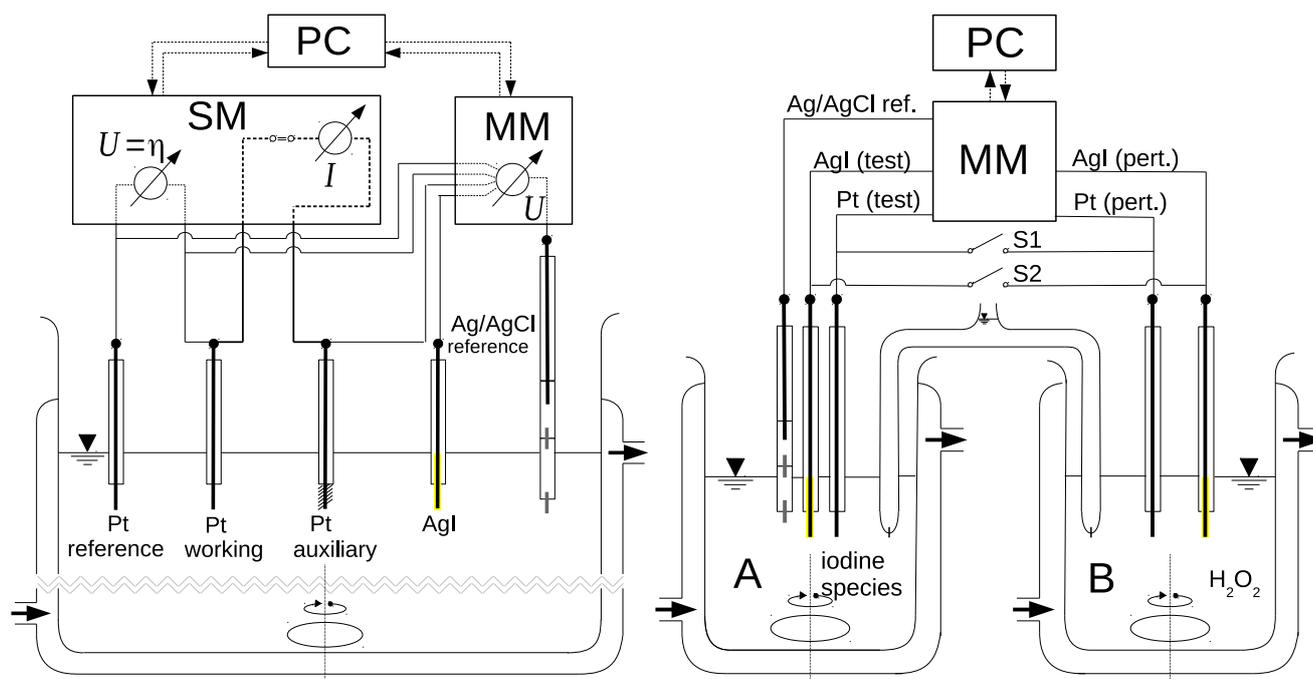


Figure 1: Symbolic diagram of the apparatus applied in the potentiometric and in the exchange current measurements (left) and schematic drawing of the apparatus to measure mixed potentials (right).

2.2 Coupling of pH oscillators

A scheme of the experimental setup of the measurements of the coupling in a one volume homogeneous reactor can be seen in figure 2. In these measurements both the master and the slave systems were in the same reactor in the same phase. We were able to observe the state of the pH oscillator – master system – and the carbon dioxide equilibrium – slave system – by following the pH and the carbon dioxide concentration.

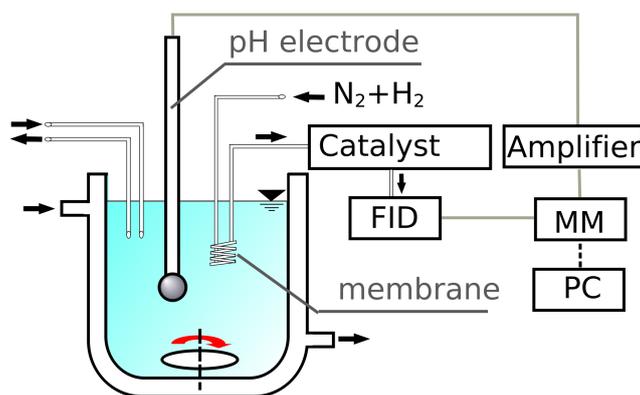


Figure 2: Sketch of the experimental setup of the measurements of the coupling in a one volume homogenous reactor. Catalyst, Ni catalyst; FID, flame ionization detector; MM, multimeter; PC, computer. Membrane is made of silicon, which is fully penetrable for the produced carbon dioxide.

Figure 3 shows the schematic drawing of the spatially separated pH oscillators. This system has three reactors. We measured the pH–time curve in each reactor. The first reactor contains the master system, the bromate–sulfite–hydrogen carbonate pH oscillator, that drives the slave system, a peroxide pH oscillator. The interaction between the spatially separated master and slave system was created through a silicone membrane between the slave system and the waste stream of the master system. The third reactor – in which the pH was measured – was created from the waste stream of the master reactor after the mass transfer between the master and the slave system.

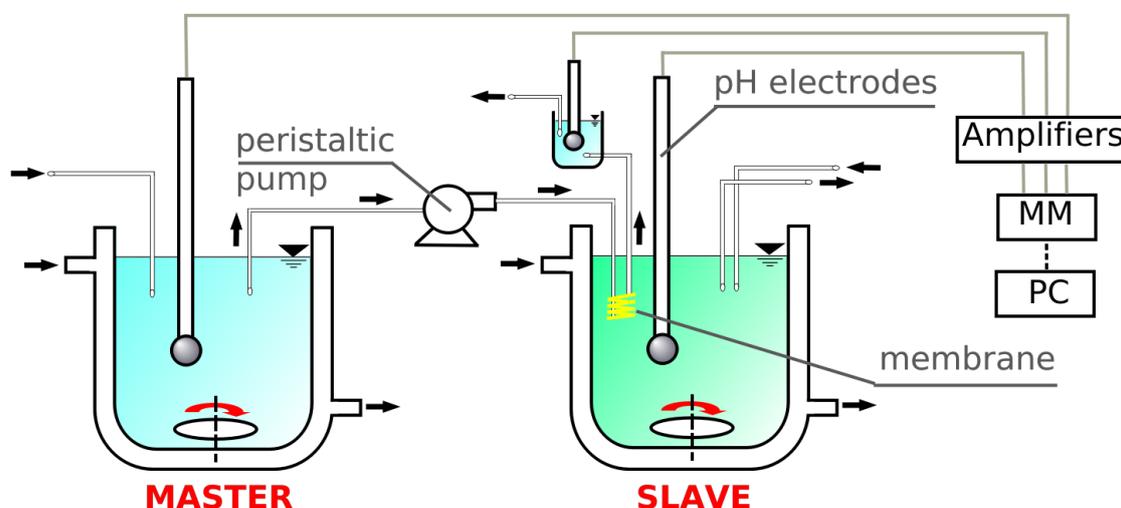


Figure 3: A schematic drawing of the spatially separated pH oscillators. MM: multimeter, PC: computer.

2.3 Examination of I₂O

In figure 4.a the sketch drawing of the apparatus can be seen, which was used to measure the volatility of I₂O. The I₂O containing solution was placed in the reactor of the right side and the air space was connected with the air space of the iodide solution containing reactor on the left side. The stream of I₂O is shown with gray arrows. It can occur an opposite stream too: in the case when the solvent of I₂O is concentrated sulfuric acid water can diffuse in the opposite direction.

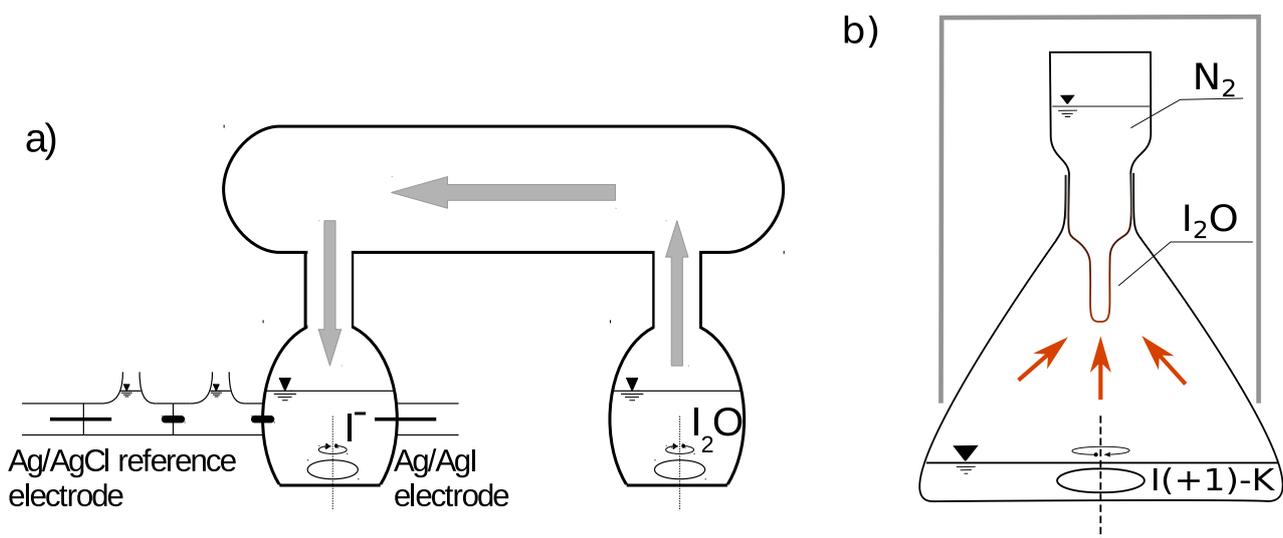


Figure 4: Schematic drawings of the apparatuses: a) The examination of the volatility of I_2O . The reactor on the right side contains 1 mL I_2O solution in concentrated sulfuric acid or in dichloromethane (DCM). The reactor on the left side contains a iodide solution in 25 mM sulfuric acid, which concentration was followed with an Ag/AgI electrode against an Ag/AgCl reference electrode which was filled with 0.1 M KCl. The salt bridge and the reference electrode contained 25 mM sulfuric acid as well. Both reactors were thermostated at $\Theta = 25\text{ }^\circ\text{C}$ and their gas space were connected according to the figure so the two reactors perform a closed system together. b) Sketch of the „cold finger” which is used to prepare the I_2O . The cold finger was placed over a I_2O containing solution and it was cooled with liquid nitrogen.

The symbolic diagram of the „cold finger” which was used in the preparation of I_2O can be seen in figure 4.b. At the bottom of the flask concentrated sulfuric acid I_2O solution was mixed with a teflon stirrer. The cold finger reaching in the air space was cooled with liquid nitrogen. The flask was connected with the nitrogen container through a glass grinding to exclude water. The gray bell in the figure illustrates the insulation around the apparatus.

The function of the insulation was - beside the warmth insulation - to keep the material in dark. Iodine species are often light sensitive therefore, we could prepare I_2O in the dark. Furthermore the bell was able to reduce the icing of the outer surface of the flask which makes it easier to observe the material. The nitrogen gas produced in the boiling headed out at the bottom of the bell reducing the inflow of vapor.

3 Results

3.1 HOI vs HOIO selectivity of an Ag/AgI electrode

TO STUDY the question of the HOI versus HOIO selectivity of the electrode, we prepared a HOIO sample with less HOI contamination. Moreover, the sulfuric acid concentration was increased to 1 M, where the iodous acid disproportionation is slower, and the rate of heterogeneous corrosion reaction, consequently, the corrosion potential due to HOIO could be higher.

In a first series of experiments the response of the electrode was followed after the injection of HOIO, and it was assumed that the potential jump was due dominantly to HOIO and the much smaller HOI content had no significant effect. With that assumption HOIO gave a close to Nernstian potential response, analogous to the one observed with HOI, but the HOIO calibration line was considerably below that of the HOI.

Such a behavior could be explained with the corrosion potential theory and could be described by a Nicolsky–type equation¹² for the electrode potential where both HOIO and HOI are fast corrosive agents. Nevertheless, an alternative explanation, that the observed close to Nernstian response was still due to the minor HOI contamination of the HOIO sample, could not be excluded either.

Thus, in a second series of experiments, to eliminate safely any interference due to HOI, we applied also resorcinol, which is a very effective HOI scavenger. That way it was possible to prove convincingly that a nonzero corrosion signal caused by HOIO really exists. However, that signal was found to be rather weak and the experiments gave a non–Nernstian calibration diagram with a slope of about 20 mV/decade, characteristic for slow corrosion processes¹³.

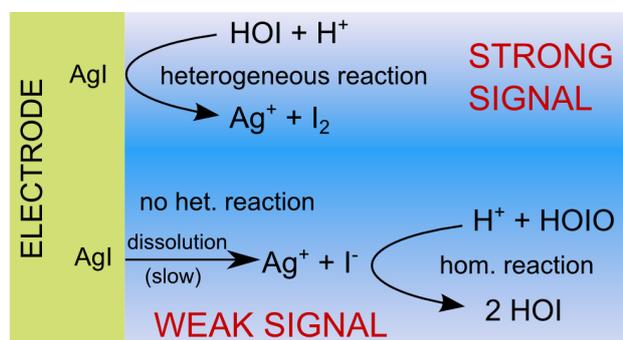


Figure 5: Illustration of the heterogeneous reactions.

the process seemed to be an ideal testing ground for the GN equation. The kinetics of the disproportionation of HOIO was simulated, and the calculated electrode potential versus time curves were compared with the experimental ones.

Due to the non–Nernstian response for HOIO, the HOI versus HOIO selectivity cannot be characterized by a usual Nicolsky–type selectivity coefficient. If we assume, however, that the corrosion of the electrode by HOI and HOIO proceeds independently then a generalized Nicolsky–type (GN) equation can be derived. To test that formula, we wanted to compare measured and calculated electrode potentials in different HOI–HOIO mixtures.

In the course of the disproportionation process of HOIO, the HOI/HOIO concentration ratio is changing continuously. It starts from a very low value to reach high values later. Thus,

¹²D. G. Hall, *The Journal of Physical Chemistry* **100**, 7230–7236 (1996).

¹³Z. Noszticzius, E. Noszticzius, Z. A. Schelly, *The Journal of Physical Chemistry* **87**, 510–524 (1983).

It was found, however, that disregarding the first 50–70 s long transition period (which was due to the response time of the electrode) calculations assuming that the electrode responds to HOI only gave better fittings of the experimental and calculated curves than calculations applying the GN equation. This result suggests that the hypothesis of the GN equation, the independence of the corrosion processes, fails, and HOI is able to prevent the electrode somehow from responding to HOIO, even if the latter is present in much higher concentration than HOI. In other words, when HOI is present, the electrode potential is determined by that component exclusively.

That conclusion was also proven by a direct experiment where HOIO was injected in a relatively high concentration into a 30× more dilute HOI solution without causing any detectable instantaneous change of the electrode potential. As in numerous oxyiodine reaction systems (like in BL or BR oscillators and their subsystems) the concentration ratios are just the opposite (HOI is usually present in much higher concentrations than HOIO), we can conclude that in such systems the electrode potential is governed by HOI selectively and any interference due to HOIO can be neglected.

3.2 Platinum as a hypiodous acid–iodine redox electrode



OUR MAIN aim was to study the potential response of the Pt electrode for oxyiodine species, especially for HOI, because HOI can appear periodically in the BR reaction. It is well known that in the presence of I_2 and I^- , the potential of the Pt electrode can be expressed with the Nernst equation. However, when HOI is present at high concentration in a mixture of I_2 , I^- , and HOI, the rapid iodine hydrolysis equilibrium drives $[I^-]$ to a very low value. In this case, although the above formula is still valid from a thermodynamic point of view, it is questionable whether a stable electrode potential can be measured when the potential-determining iodide ion concentration is so low.

To test the Pt electrode in this respect, first we decided to titrate a HOI solution with I^- in the simultaneous presence of Pt and AgI indicator electrodes. Before the equivalence point, $[I^-]$ is low because of the high $[HOI]$, and thus a stable electrode potential in this region would suggest that in this case Pt potentials are not controlled directly by the small I^- concentration and thus by the I_2/I^- redox couple but rather by the HOI/I_2 redox couple.

In the case of obtaining stable over-HLP Pt electrode potentials in the presence of HOI, we also aimed to measure the EMF_{Pt} vs $\lg \frac{[HOI]}{[I_2]}$ calibration line. I_2 –HOI mixtures, however, were not prepared by adding HOI to an iodine solution. The HOI solution was prepared with silver ion addition to the iodine solution. By using Ag^+ ions instead of $I(+1)$ solutions in DCM, uncertainties due to a $I(0)$ or $I(+3)$ contamination of the $I(+1)$ solution do not matter. HOI concentrations can be calculated from the amount of the added Ag^+ ions regarding the AgI solubility and iodine hydrolysis equilibria.

Iodine solutions always have some iodide contamination. We decreased this initial iodide content with addition of $AgNO_3$ and the remaining small iodide content was taken into account in the fittings. In the fittings of the calibration lines we assumed an ideal Nernstian response of the platinum electrode so we used the theoretical slope of 59,16 mV/decade. The experimental calibration lines – produced in this way – were close to the theoretical ones. However, we experienced a small shift in the intercepts due to the reference electrode. This shift was corrected first with an iodide calibration of the Ag/AgI electrode and finally we used the platinum electrode I^-/I_2 calibration line to obtain more reliable results. With this correction the distance of the theoretical and the experimental lines became 1.6 mV which is comparable with the experimental error.

In the case of the Ag/AgI electrode from the intersection of the I^- and the Ag^+ calibration lines above and under the SLP the silver iodide solubility product is quantifiable. On an analogous way we were able to measure the iodine hydrolysis constant from the intersection of the I^-/I_2 and the HOI/I_2 calibration lines above and under the HLP in the case of the platinum electrode. We obtain a rather good agreement with earlier measurements: $K_H^0 = (4.97 \pm 0.2) \cdot 10^{-13} M^2$.

It can be seen from the calibration lines that above the HLP iodine is the oxidized form and under the HLP iodine acts as the reduced form of the redox couple. According to that, the electrode potential decreases with an increasing iodine concentration above HLP, but under HLP the electrode potential increases with the iodine concentration. We observed this effect experimentally: we added iodine to a HOI and a iodide solution and we got the expected potential response. Furthermore, we proved that the decrease in the potential above the HLP was more significant which could be explained with the iodide content of the iodine solution.

A more direct possibility to prove that below and above the HLP different redox couples control the Pt potential, is to perform exchange current measurements. In the course of a titration of HOI by I^- in the presence of a relatively high I_2 concentration, the I^- concentration increases and the HOI concentration decreases monotonically, whereas the I_2 concentration is practically constant (its increase is relatively small). Thus, if the exchange current and the Pt potential were determined by the concentration of the I^- and I_2 species, then the exchange current should increase monotonically during the whole titration.

However, assuming that above the HLP the actual potential-controlling species are HOI and I_2 , the exchange current should decrease monotonically, reflecting the decreasing HOI concentration until the HLP, below which I^- and I_2 species take over control. We found in the experiments that exchange current is not a monotonic function but it has a minimum at the HLP. Thus, assuming that below and above the HLP the actual potential-controlling redox couples are not the same, this phenomenon became understandable.

Furthermore, we examined the effect of other oxidine species which play important role in the BR reaction such as iodous acid and iodate. $I(+3)$ and $I(+5)$ could influence of the Pt electrode potential if their reduction would be fast enough on the surface of the electrode. We repeated the experiment what we performed in the case of the Ag/AgI electrode: iodous acid and iodate was injected in a HOI-iodine solution in a great excess. However, we did not observe any increase in the potential, so we consider that the rate of this processes is negligible compared to the HOI reduction.

In the BR reaction, however there is another component which can influence the platinum electrode potential: H_2O_2 . According to that we examined the perturbing effect of H_2O_2 in the case of the Pt and the Ag/AgI electrode as well. In these experiments one test electrode was placed into sulfuric acid of 25 mM which contained oxidine species and the perturbing electrode – according to the BR reaction – was immersed into 0.66 M H_2O_2 . With this spatial separation we were able to measure mixed potential without allowing reaction between the iodine/oxyiodine species and H_2O_2 . On the other hand we were not able to observe such a perturbing effect below the HLP.

In these experiments when we connected electrically the test and the perturbing electrodes a mixed potential was measured. According to our results in the case of the Ag/AgI electrode the perturbing effect of the H_2O_2 is negligible above and under the SLP as well. However the Pt electrode potential above the HLP – where the potential is determined by the HOI/ I_2 redox couple – was significantly modified due to the electrical connection so in the BR reaction the perturbing effect of the H_2O_2 can not be excluded.

Finally, we measured the Pt and the Ag/AgI electrode potential in the BR oscillating reaction simultaneously. We showed that both the Pt and the Ag/AgI electrode potential exceed their equivalence point: the HLP and the SLP. However, while the Ag/AgI electrode is sensitive exclusively to the HOI, in the case of the Pt electrode above the HLP one has to take into account the effect of H_2O_2 as the Pt electrode shows a mixed potential.

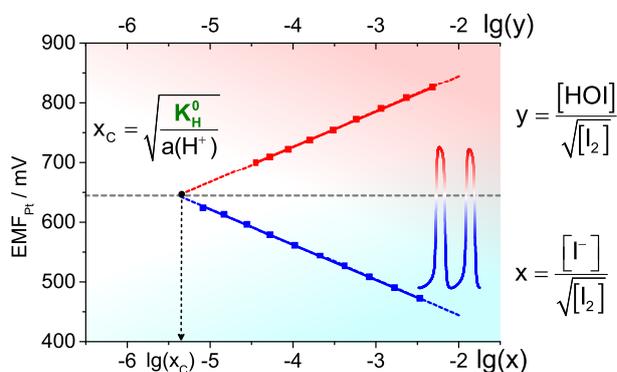


Figure 6: Calibration lines of the Pt electrode.

3.3 Preparation of diiodine monoxide

THE Cl_2O and the Br_2O were prepared previously¹⁴. Their decomposition temperature decrease with the increasing of the mass of the halogen atom. According to that we can expect that I_2O is at low temperatures. Based on the properties of the analogous halogen species diiodine monoxide should be a brown solid material which decomposes at higher temperatures.

We prepared I_2O in concentrated sulfuric acid with the reaction between iodine and iodate. In a pure sulfuric acid Gillespie assumed the existence of the following species: $(\text{IO})\text{HSO}_4$, I_3^+ , I_5^+ ¹⁵. However, we used 96% sulfuric acid which contains higher H_3O^+ concentration, which makes possible to observe I_2O : $(\text{IO})\text{HSO}_4 + \text{I}_3^+ + 2 \text{HSO}_4^- + \text{H}_3\text{O}^+ \rightleftharpoons 2 \text{I}_2\text{O} + 3 \text{H}_2\text{SO}_4$.

We have observed a $\text{I}(+)$ species evaporating into the gas phase from the concentrated sulfuric acid I_2O solution prepared in the following way. The air space of the concentrated sulfuric acid I_2O solution was connected with the air space of a iodide containing reactor and the iodide concentration in the reactor was followed with a iodide selective electrode. During the measurement, the iodide concentration was decreased due to the $\text{I}^+ + \text{I}^- \longrightarrow \text{I}_2$ reaction. The electromotive force–time diagram looked like a titration curve which can be explained with a constant $\text{I}(+)$ inflow. According to that, we can assume an equilibrium I_2O concentration in the concentrated sulfuric acid solution and the diffusion of I_2O through the gas phase to the iodide containing reactor which decreases its $[\text{I}^-]$ concentration.

Both Cl_2O and Br_2O are soluble in carbon tetrachloride. I_2O can be extracted from concentrated sulfuric acid with DCM. When we measured the volatility of I_2O from a dichloromethane (DCM) solution the I_2O concentration was found to be even higher than in the case of concentrated sulfuric acid. Based on this experiment we can assume that I_2O is well soluble in DCM and it was able to shift the equilibrium in the concentrated sulfuric acid to the formation of I_2O during the extraction.

Oxiodine species are highly reactive so they might be able even to react with DCM. However according to NMR measurements we concluded that DCM does not take part in a chemical reaction so it acts solely as a solvent in the extraction from the sulfuric acid phase.

In concentrated sulfuric acid we were able to measure I_2O in the mass spectrum. We observed that water addition in a small amount can increase the size of the I_2O peak in the mass spectrum which confirms our previous assumption that the presence of a small amount of water can shift the equilibrium to the formation of I_2O .



Figure 7: I_2O on the „cold finger”.

¹⁴Balard, *Ann. Chim. Phys.* **57**, 225 (1834).

¹⁵R. J. Gillespie, J. B. Senior, *Inorganic Chemistry* **3**, 972–977 (1964).

Since we measured a considerable amount of I_2O in the gas phase above the concentrated sulfuric acid solution we tried to prepare this species purely from the gas phase. A „cold finger” cooled with liquid nitrogen was placed above the I_2O solution and I_2O was formed on this cooled surface. The color of the material seemed to be light brown at the beginning of the experiment and it became darker with the thickening of the layer. The prepared material – similarly to the Br_2O – decomposed on a low temperature and after the disappearance of the liquid nitrogen – in the case of a thin layer – it disappeared without any trace. In the case of a thicker layer we were able to observe black iodine crystals on the surface of the cold finger after the decomposition which suggests that I_2O – similarly to the analogous halogen species – decomposes to iodine and oxygen.

3.4 Coupling of pH oscillators



WE SHOWED a new approach and provided a new terminology to study and analyze the coupling strategy between driving (master) and slave systems. In the presented examples the driving system is a pH oscillator and the slave subsystem is a pH-dependent equilibria.

Design strategies in previous studies published in the literature have been focused on oscillatory dynamics of the target species participating only in the chemical equilibria (slave system) and on diminishing the feedback and the effect of the chemical equilibria (slave system) on the main driving system¹⁶. The main characteristic of this, so-called master–slave, coupling is that the master system (pH oscillator) drives the phenomenon, and the slave system (equilibrium reaction) should not interfere and change the main characteristics of the master system.

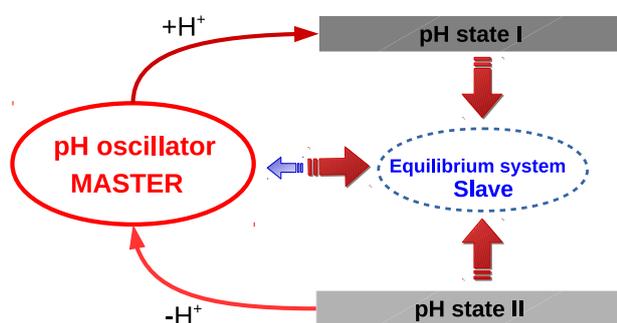


Figure 8: Interaction between the master and the slave system.

of the oscillations.

The coupling strength can be varied and controlled by addition of control species (in this case the hydrogen carbonate), which react with H^+ ions reversibly, thus affecting its effective concentration in the system. At low concentration of the control species the feedback from the slave system to the driving one can be seemingly negligible (but definitely accountable); however, the oscillatory behavior of the target species (participating only in the slave system) can be strong enough to be measured and detected. This has been considered as master–slave coupling, and usually this strategy has been followed when coupled systems were designed in the past. By increasing the coupling species concentration, the feedback from the slave system to master system is more pronounced resulting in

We studied a coupled system, the bromate–sulfite pH oscillator was coupled to the carbonate–carbon dioxide equilibrium. From our investigations, we revealed that in one-volume homogeneous chemical reaction network pure master–slave coupling cannot be possible through a single coupling species, which is incorporated both in the kinetics of the master and slave subsystem. Especially, if the coupling species is directly involved in the autocatalytic pathway of the oscillator (such as H^+ in a pH oscillator), even a small perturbation of its concentration made by the slave system might result in a significant feedback on the parameters

¹⁶K. Kurin-Csörgei, I. R. Epstein, M. Orbán, *Nature* **433**, 139–142 (Jan. 2005).

significant changes in the characteristics of the master system.

However, there is no clear borderline between the master-slave and peer-to-peer coupling because the transition is continuous between them. Therefore, the manner of the coupling is somewhat „user-defined” in a wide range of the parameters. In particular above a critical concentration of the coupling species (due to its H^+ binding capacity) the oscillatory behavior of the system can vanish.

We found in the experiments as well as in the numerical model simulations that the system shows critical behavior when the inflow concentration of the control species reaches a threshold concentration. This threshold inflow concentration defines the point where the coupling is clearly peer-to-peer type since a small variation of the concentration results in a bifurcation from the oscillatory state to a stationary one. Additionally, our system is the first one in which oscillations of a gas phase species has been successfully realized using coupling strategy between a pH oscillator and a pH-dependent equilibrium.

We highlight the importance of the controlling the feedback strength, using this approach we can fine-tune and change the characteristics of the driving system, which otherwise would be hard to be realized. For instance, the amplitude and the time period of pH oscillators can be modified by varying the concentration of the reagents, flow rate, and other experimental parameters (temperature, etc.); however, the ratio of time that the system spends at low and high pH states cannot be achieved by this way. To achieve it, such coupling strategy would be a perfect candidate for doing it, and in this way, new oscillatory systems can be designed that have different characteristics compared to the original oscillatory systems.

In a one-volume homogeneous reactor – due to the common chemical environment – the perfect master-slave coupling cannot be achieved. There is always some feedback from the slave to the master system. To completely exclude this feedback we used a strategy – which is very general in electrochemistry – we spatially separated the two system. In practice, the waste stream of the master CSTR reactor was flown through the slave CSTR reactor in a silicon tube (silicon membrane). In this way the slave system has an interaction with the waste stream of the master reactor, but the state of the master system will be independent from the slave system. With the complete exclusion of any feedback we created a *perfect master-slave coupling*.

A long time period bromate-sulfite-hydrogen carbonate pH oscillator was chosen as a master system and a sensitive short time period hydrogen peroxide-sulfite-hydrogen carbonate pH oscillator was used as a slave system. In the neutral state of the master system the slave system showed regular oscillations although in the acidic state of the master system irregular oscillations were observed in the slave system. This is because carbon dioxide is able to go through the silicone membrane so the high amount of carbon dioxide – which is created in the acidic state of the master system – can perturb significantly the slave system. Contrarily in the neutral state of master system the carbonate-hydrogen carbonate-carbon dioxide equilibrium is shifted to the hydrogen carbonate, so the master system contains less free carbon dioxide consequently the slave system can oscillate unperturbedly.

During the examination of the waste stream of the master reactor we realized that the slave system reacted directly to the state of this solution and not to the state of the master system. This is because the slave system has not a direct interaction with the master system, but it is connected with the waste stream through a membrane. Furthermore the solution in the silicon tube has a small volume, the slave system has a strong effect on it. According to that the state of the waste stream and the slave system changed in the same time differently from the master system.

As a summary we can say that with spatially separated coupled pH oscillators we were able to prescribe – on an autonomous way – which time should the slave system oscillate regularly or irregularly. This prescribed time intervals can be modified with fine tuning the master system and with the coupling strength we can control the state of the slave system.

This approach is not limited to pH oscillators, this control and coupling strategy could be also used in other chemical or biochemical network systems, where the driving oscillation manifests in other forms of oscillation (e.g., redox potential).

4 Theses

1. I have calibrated the Ag/AgI electrode for pure iodous acid, by excluding any hypoiodous acid contamination. The potential answer of the Ag/AgI electrode was non-Nernstian, the calibration curve had a lower slope. I have also shown that the electrode was not sensitive to iodous acid in the presence of hypoiodous acid. Based on these observations I conclude that *the Ag/AgI electrode has a high HOI vs. HOIO selectivity [S1]*.

2. I have recognized that the *Pt electrode can measure the HOI/I₂ redox couple [S2]*. The measured calibration curve – within experimental error – was the same as the calculated one. Based on exchange current measurements I have proved that above the hydrolysis limit potential the electrode potential of the Pt electrode is determined directly by the HOI/I₂ redox couple.

3. I have determined the value of the iodine hydrolysis constant with a *new, electrochemical method*, based on the intercept of the I₂/I⁻ and the HOI/I₂ calibration lines of the Pt electrode [S2].

4. *I have prepared I₂O* with the reaction of iodate and iodine in a concentrated sulfuric acid medium. This is the first preparation of I₂O, a species whose existence was just a theoretical possibility before. I have detected I₂O in the concentrated sulfuric acid phase with electrochemical methods and with mass spectrometry. I have shown that I₂O is a volatile species, and with liquid nitrogen cooling I have prepared it in solid state.

5. I have introduced a new approach to study and analyze *coupled chemical systems [S3]*. I have shown that with a fine tuning of the coupling species' concentration we can turn master–slave into peer–to–peer coupling. I have achieved the *perfect master–slave coupling with spatially separated systems*. I coupled the bromate–sulfite–hydrogen carbonate pH oscillator to the hydrogen peroxide–sulfite–hydrogen carbonate pH oscillator using a silicon rubber membrane, as an example for the perfect master–slave coupling. The coupling was established with the silicon rubber membrane which has a high carbon dioxide permeability.

*„I would have written a shorter letter,
but I did not have the time.”*

— Blaise Pascal

5 Application possibilities

Application possibilities of the Ag/AgI and the Pt electrodes



HYPOIODOUS ACID plays an important role in the global iodine circulation, and HOI is also a component in the waste streams of nuclear reactors. Both process has a great environmental significance so it would be necessary to create a method to measure the atmospheric HOI concentration.

Since both the Ag/AgI and the Pt electrode is able to measure HOI it is possible the create a sensor with this electrodes which is able to follow the *atmospheric HOI – or I₂O – concentration*. This measurement – being a plain potentiometric measurement – would be simple and cheap. The electrodes react sensitively to the concentration changes around their inflexion point. If HOI goes through a – silicone or a teflon – membrane, then it would be able to react with a small changeable iodide content and small atmospheric HOI concentrations would become measurable. This small iodide concentration can be produced electrochemically from an iodine solution or with a dilute iodide solution flowing through the sensor.

One another possibility – which was the aim of our research – to directly use the electrodes in *the kinetic investigation of the iodine oscillators and their subsystems*. The selectivity of the electrodes was investigated in these systems, so we collected the most information about their behavior in these circumstances.

The electrodes can be used analogously in other halogen systems too. We observed a similar behavior of the Ag/AgBr and the Pt electrode in the bromate oscillators, so it can be assumed that with these electrodes the *HOBr concentration* can be followed.

Utilization of the I₂O

The I₂O was used previously in kinetic models – so with our preparation in a solid form – one can accept these models as more realistic ones. Besides of the theoretical importance the preparation of I₂O can have some practical significance too. Namely, we can get a very pure iodination agent because in the reaction of I₂O with water we can get hypoiodous acid so we can produce a *pure iodination agent – I⁺ –* without byproducts.

Unfortunately I₂O decomposes at a low temperature and it is sensitive to moisture so in practice it is difficult to use. However I₂O remains stable in a dichloromethane solution at room temperature so chemists can use it in DCM solution in iodinating reactions.

Application of the master–slave systems

We observed in the spatially separated master–slave systems that the solvent – flowing in the silicon tube – take part in a peer–to–peer coupling with the slave system. This observation makes it possible to create various sensors. If the system – which is separated with the membrane – there is a self-accelerating reaction, therefore a small change in the slave system can cause a big change in this separated system which is flowing in the tube. With *chemical amplification* it is possible to follow small changes in a system. It can be used in an industrial control process the concentration of a component should not exceed a given threshold.

In our case if we keep the pH constant in the slave system, the sensor – the solvent flowing in the silicon tube – would be sensitive to the carbon dioxide concentration changes; otherwise with a fix carbon dioxide concentration it would be able to measure small pH changes in the slave system. If we change the membrane or the coupled systems it is possible to measure other components as well with the exploitation of the chemical amplification.

Publications related to the dissertation

- S1. G. Holló, K. Kály-Kullai, T. B. Lawson, Z. Noszticzius, M. Wittmann, N. Muntean, S. D. Furrow, G. Schmitz, HOI versus HOIO Selectivity of a Molten-type AgI Electrode. *The Journal of Physical Chemistry A* **118**, PMID: 24892210, (IF = 2.847), 4670–4679 (2014).
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- E1. T. Keszthelyi, G. Holló, G. Nyitrai, J. Kardos, L. Héja, Bilayer Charge Reversal and Modification of Lipid Organization by Dendrimers as Observed by Sum-Frequency Vibrational Spectroscopy. *Langmuir* **31**, PMID: 26099064, 7815–7825 (2015).
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- E7. G. Holló, Á. Leelőssy, R. Tóth, I. Lagzi, *Tactic Droplets at the Liquid–Air Interface*, in: *Self-organized Motion, Physicochemical Design based on Nonlinear Dynamics* (Royal Chemical Society, 2018).

Oral presentations

- O1. G. Holló, Hipójódossav szelektív mérése AgI és Pt elektróddal az oszcilláló Briggs–Rauscher reakcióban és alrendszeriben. *Oláh György Doktori Iskola Konferenciája*, Budapest (2014.02.06.).
- O2. G. Holló, E. Tóth-Szeles, J. Horváth, R. Szűcs, H. Nakanishi, I. Lagzi, Time-programmed self-assembly. *The 7th KIT WORKSHOP ON ADVANCED POLYMER MATERIALS and FIBER SCIENCE*, Kyoto Institute of Technology, Kyoto, Japan (2017.03.27.).
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Poster presentations

- P1. G. Holló, E. Tóth-Szeles, J. Horváth, R. Szűcs, H. Nakanishi, I. Lagzi, Time-programmed self-assembly. *MaCKiE (International Conference on Mathematics in (bio)Chemical Kinetics and Engineering)*, Budapest (2017.05.25–27.).
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