

A New Chemical Oscillator in a Novel Open Reactor: The ClO_2 – I_2 –Acetone System in a Membrane Fed Stirred Tank Reactor

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The title reaction was carried out in a new type of semibatch reactor, where iodine or both iodine and chlorine dioxide are fed to the stirred bulk of the reactor through thin and selective silicon rubber membranes. For model calculations the iodine inflow rate and the pseudo-first-order rate constant of the iodide production from iodine were determined experimentally. All other reactions and rate constants were taken from the literature. The period and the duration of the experimentally found and theoretically predicted oscillations agree rather well. An exact electrochemical interpretation of the amplitude of the electrode potential oscillations requires further research.

Introduction

Nonlinear chemical systems maintained far from equilibrium and producing symmetry-breaking instabilities are in the focus of current interest. An intensively studied example is the chlorite–iodide–malonic acid (CIMA) reaction^{1–3} producing sustained oscillations (symmetry breaking in time) in a continuously fed stirred tank reactor (CSTR).⁴ The same reaction gives different stationary and moving patterns^{5–7} (that is symmetry breaking in space) in a continuously fed unstirred reactor (CFUR). As the above examples show there are two important prerequisites to observe such unusual or “exotic” phenomena: (i) a nonlinear chemical reaction with positive and negative feedback loops (that is with a rather complex mechanism) and (ii) a continuously fed stirred or unstirred reactor to maintain the complex chemical system far from equilibrium. Thus, the search for new symmetry-breaking instabilities in chemistry is partly a search for new complex reaction systems^{8,9} and partly a search for new types of open reactors.^{10–12} Here we report a new chemical oscillator, the chlorine dioxide–iodine–acetone system, which displays its exotic dynamical behavior in a new type of reactor where iodine alone or both iodine and chlorine dioxide are fed into the reactor via selective membranes. We suggest the names CIA for the new reaction and MSTR for the new reactor.

The motivation of the present research was the recent discovery of a new chemical oscillator: the chlorine dioxide–iodomalonic acid–chloride or CIMA–Cl reaction.¹³ The CIMA–Cl reaction shows long-lived oscillations in a batch reactor, which is rather unusual. Before the discovery of the CIMA–Cl system only the Belousov–Zhabotinsky reaction¹⁴ and the Bray reaction¹⁵ were known to oscillate in a batch reactor for a longer period. Furthermore, the concentrations of the main reactants in the CIMA–Cl system are rather low: they are in the millimolar range and below. Thus, the system is a promising candidate for mechanistic studies. On the other hand, the role of iodomalonic acid and chloride ions is not quite clear. The

following hypothetical reaction sequence can be suggested, however. As the iodination of malonic acid is a reversible reaction,¹⁶ iodomalonic acid is able to hydrolyze, producing hypoiodous acid. It is also known that hypoiodous acid can react with chloride ions to form iodine chloride.¹⁷ If we assume that ICl is able to react with malonic or iodomalonic acid to form chlorinated organic products and iodide ion, then the role of iodomalonic acid and chloride is simply to maintain a constant inflow of ICl, which, in turn, is a source of iodide ions. We tried to mimic the combined role of iodomalonic acid and chloride ions with a constant inflow of elementary iodine into a reactor where besides chlorine dioxide some acetone is also present. The iodination of acetone can also form iodide just like that of malonic acid. Acetone was chosen instead of malonic acid because the latter is more capable to other reactions besides iodination, and we wanted to create a system as simple as possible. In this new oscillatory CIA reaction both the platinum and the iodide selective electrodes display potential oscillation which are rather close to the ones detected in the CIMA–Cl system regarding the observed frequency and amplitude of the oscillations as well.

The most important new feature of the reactor design reported here is the application of a highly permeable and selective silicon rubber membrane,¹⁸ the preparation of which will be discussed later. Iodine permeates via this membrane to the reaction mixture. Actually, from a theoretical point of view, our MSTR is a new variant of the so-called “dubbed semibatch reactor”¹⁹ type used extensively by Orbán, Rábai, and Epstein.^{20–22} In a semibatch reactor there is an inflow but no outflow, which is a major difference from a CSTR. A technical limitation of the semibatch reactors is, however, that the reaction volume is increasing in time due to the constant inflow. An advantage of the present MSTR design is that this effect is minimized here because no solvent inflow is associated with the selective permeation of iodine or chlorine dioxide. Thus, a far-from-equilibrium situation can be maintained for a longer time in an MSTR and with relatively simple means: no pumps are required. Only a reservoir of elementary iodine is needed, which is separated by the permeable membrane from the stirred bulk of the reactor.

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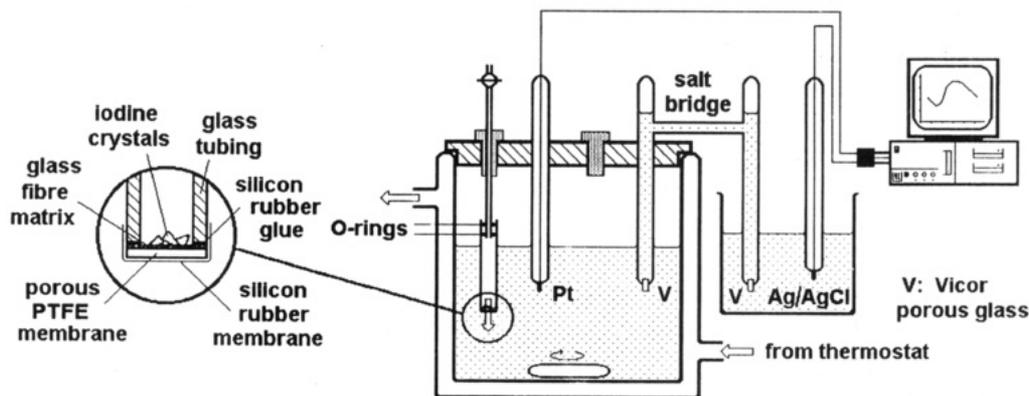


Figure 1. Scheme of the membrane fed stirred tank reactor (MSTR) and some parts of the experimental setup. For the sake of simplicity only one measuring electrode and one permeator are shown. During the measurements the system was placed in a black box to exclude light since the reaction and the iodide electrode are light-sensitive.

Model calculations for the CIA reaction were performed by applying the Citri–Epstein²³ and a part of the Lengyel–Rábai–Epstein² mechanism for the inorganic subset of the CIMA reaction together with the iodination of acetone and by assuming a constant inflow of elementary iodine. The numerical values of the rate constants were taken from a recent series of papers.^{24–26} The rate of the iodine inflow and the pseudo-first-order rate constant of the iodide production from iodine were determined experimentally. The model calculations show a rather good qualitative agreement with the experimental observations.

Experimental Section

Chemicals. Gaseous chlorine dioxide and ClO_2 solutions were prepared by the method²⁷ of Lengyel et al.^{2,28} The concentration of the ClO_2 stock solution was determined with ascorbinometric titrations as described previously.¹³ Solutions of chlorine dioxide were freshly prepared from the stock, which was kept refrigerated. The stock solution was stable: no measurable change in its concentration was observed for several months. Iodine, acetone, and sulfuric acid applied in the experiments were of reagent grade and used without further purification.

Apparatus. The Role of the Iodine Permeator. The experimental setup is depicted in Figure 1. A major new feature of the reactor design applied here is a membrane permeator producing a constant inflow of iodine to the reactor. The permeator itself is a small glass vessel containing a few crystals of elementary iodine. It is separated from the magnetically stirred bulk of the reactor by a thin silicon rubber membrane, which is highly permeable for iodine vapors. While the vapor pressure of the elementary iodine is close to its equilibrium value inside the permeator vessel, it is orders of magnitude smaller outside. Thus, the driving force of the permeation, the chemical potential gradient for iodine across the membrane, is determined mainly by the larger pressure inside the permeator, which is constant due to the thermostated environment ($25\text{ }^\circ\text{C}$). Consequently, the permeator works as a constant iodine current generator; its current can be determined in separate experiments.

Other Possible Effects of the Permeator. The silicon rubber membrane is also permeable for vapors of water, chlorine dioxide, and acetone. Thus, at least in theory, these components are able to permeate in a “backward” direction, that is, from the liquid phase in the reactor to the gaseous phase in the permeator vessel. This process stops soon, however, when vapor pressures become equilibrated at the two sides of the membrane. Such an equilibrium will be reached readily for water and acetone, which components cannot take part in

chemical reactions inside the permeator. Since sulfuric acid does not permeate via the membrane, the iodination of acetone cannot take place inside the permeator in the absence of the catalytic hydrogen ions. Moreover, there is no liquid phase inside the permeator. Under the conditions applied in our experiments, the iodine crystals remained dry during the measurements. Most probably no significant chemical reaction occurs in the gaseous phase of the permeator either. The only possible chemical process would be some unknown reaction between chlorine dioxide and iodine. Nevertheless, any loss of chlorine dioxide due to such a reaction should be negligible compared to the amount of chlorine dioxide consumed in the bulk. This is because the concentration of chlorine dioxide in the aqueous solution and, consequently, its permeation rate are low in the present experiments. In summary, the only measurable effect of the permeator device applied here is a constant iodine inflow, and any side effect, if exists at all, is negligible.

Electrodes. The potential of a platinum wire and a homemade iodide selective electrode was recorded against a silver–silver chloride reference electrode placed in 1 mol dm^{-3} (M) KCl solution. To avoid any contamination of the reacting mixture with chloride ions, a salt bridge filled with 0.001 M sulfuric acid was applied. The iodide selective electrode was prepared by coating a silver wire with silver iodide melt in a similar way as bromide selective electrodes were prepared previously.²⁹ (It is important that those parts of the platinum and the silver iodide coated silver wire that are not in direct contact with the reaction mixture must be covered evenly with an insulating material. A combination of a narrow Tygon tubing and silicon grease was applied for this purpose. To maintain the original sensitivity of the electrodes, a renewal of the silicon grease layer between the electrode wires and the covering Tygon tubing is necessary after a few months of continuous use.)

Methods. Preparation and Properties of the Permeator Cell. The body of the cell is made of a glass tubing (length 40 mm , inner diameter 5 mm , wall thickness 1.5 mm). An 8 mm diameter disc was cut from a porous Teflon membrane filter with pore size $0.45\text{ }\mu\text{m}$ (Schleicher–Schüll TE36). This is a combined material where the porous Teflon layer is mounted on a glass fiber matrix to give mechanical strength. The membrane disc with the glass fiber matrix facing to the glass tubing was glued there as can be seen in the insert of Figure 1 with a silicon rubber glue (Wacker Elastosil E43). Then a thin (few micrometers) silicon rubber membrane was placed on the Teflon membrane. The silicon membrane was produced by dripping a drop of a silicon glue solution (composition: 1 g of Elastosil E43 mixed with 1 g of *n*-hexane) on the top of a water pool in a Petri dish. The cross-linked elastic membrane was

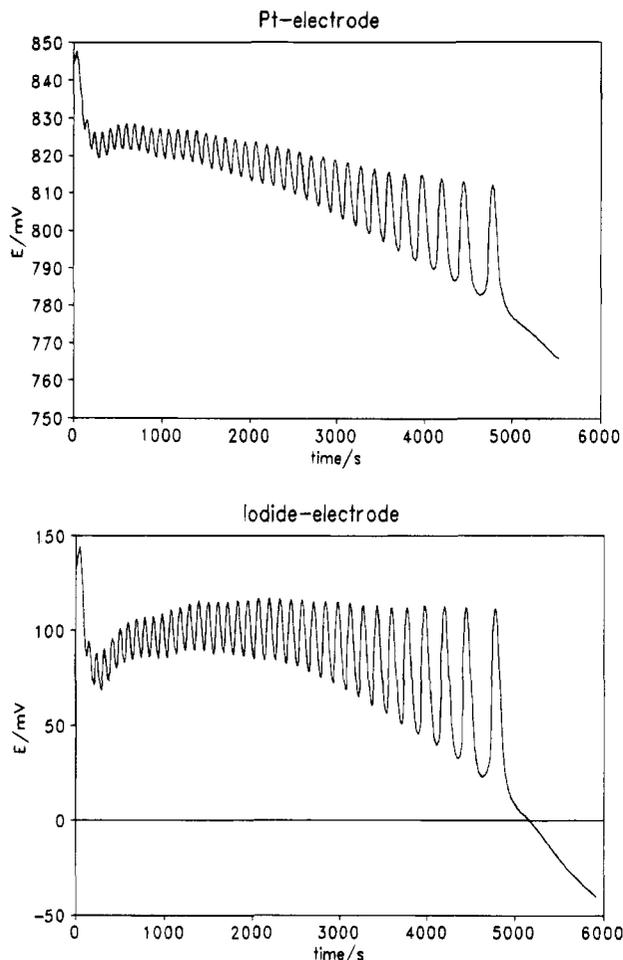


Figure 2. Potential oscillations measured in the CIA reaction with I₂ inflow only. The iodine permeator was placed into the reactor at $t = 0$. Initial conditions: $[\text{ClO}_2]_0 = 1.3 \times 10^{-4} \text{ M}$, $[\text{CH}_3\text{COCH}_3]_{0,r} = 0.545 \text{ M}$, $[\text{H}^+]_0 = 1.2 \times 10^{-3} \text{ M}$, I₂ inflow rate = $2.5 \times 10^{-8} \text{ M s}^{-1}$.

formed gradually on the surface of the water. It was removed after 1 h with a wire frame, which was placed under the water before the dripping. Permeators prepared this way provided an iodine current that were reproducible within a few percent for weeks as long as iodine crystals lasted in the device. The reproducibility can be enhanced by stabilizing the magnetic stirring. (This is because part of the mass transfer "impedance" is due to a boundary layer adhering to the membrane, the thickness of which is controlled by the stirring.) After placing the iodine crystals into the permeator, the vessel was closed with the combination of a narrow capillary and an O-ring as Figure 1 shows. Finally, the valve on the capillary was closed. This procedure prevents creating any overpressure inside the permeator, which could damage the thin silicon membrane.

Signal Recording. To record the small-amplitude potential oscillations of the electrodes, a variable offset circuit and a high input impedance amplifier (gain 20 \times) were applied for both electrodes. The signal from the amplifier was measured and recorded by a PC486 personal computer equipped with a PC Labcard (Advantech PCL-711S) and applying the Labtech Acquire software for data collecting.

Results and Discussion

Oscillations Measured in the CIA System. Figure 2 shows potential oscillations of the platinum and the iodide selective electrodes in the chlorine dioxide-iodine-acetone reaction in a membrane fed stirred tank reactor when iodine is the only

component fed continuously. The other components (chlorine dioxide and acetone) are already present in this semibatch configuration. As Figure 2 shows, oscillations start as soon as the iodine permeator is dipped into the reaction mixture containing the other reagents. When chlorine dioxide is consumed, the potential of both electrodes drops and oscillations stop. If the iodine permeator is removed from the reactor (an experiment not shown in the figure) oscillations stop abruptly within one time period even if there is enough chlorine dioxide in the reaction mixture. The oscillations resume, however, as soon as the permeator is placed back in the reactor. The frequency and range of potential oscillations of both electrodes are similar to those observed in the case of the long-lived batch oscillations in the CIMA-Cl system. Thus, at least qualitatively, the combined effect of iodine and acetone in the CIA oscillator seems to mimic the combined role of iodomalonic acid and chloride ions in the CIMA-Cl oscillator. On the other hand, it is easier to develop a mechanistic model for the CIA reaction for most of the component reactions are already known from the Citri-Epstein mechanism.²³

Mechanism of the CIA Reaction. The mechanism is shown in Table 1 together with the rate constants and with some additional reactions that are necessary to a complete mechanism of the CIA reaction. One additional reaction is the chlorine dioxide-iodide reaction, which is already known from the work of Lengyel, Rábai, and Epstein.² The other two processes are the iodine inflow and the iodination of acetone. While the chemistry of these processes is clear, for a numerical modeling we had to determine their rate constants experimentally.

Experimental Determination of the Unknown Rate Constants. *Determination of k_{13} .* Figure 3 shows the potential of the iodide selective electrode during the determination of the iodine inflow rate. The experiment is, in fact, a titration of silver ions by iodide ions generated by the iodine inflow. The iodine permeator is dipped into the reactor, which now contains a solution of silver ion, malonic acid, and sulfuric acid. The reaction volume (50 mL) and the stirring rate are the same as in the case of the CIA oscillator. The iodine inflow is converted to an iodide inflow in the iodination reaction of malonic acid, and the iodide ions generated this way titrate the silver ions. The zeroth-order rate constant of the iodine inflow can be determined simply by dividing the initial silver ion concentration by the titration time (the time elapsed from starting the iodine inflow to the time when the equivalence point is reached).

Determination of k_{14} . At higher iodine concentrations the iodination of acetone is zeroth-order for iodine since the enolization of acetone is the rate-determining step in this case. At the very low iodine concentrations characteristic for the present experiments, however, the rate-determining step is the bimolecular reaction of iodine with the enol. As acetone is in a great excess, this is a pseudo-first-order reaction for iodine. Figure 4 shows the potential of a platinum electrode during the determination of this pseudo-first-order rate constant. The potential of the platinum electrode is determined by the iodine-iodide redox couple. As the iodide concentration is approximately constant ($2.4 \times 10^{-4} \text{ M}$), the platinum electrode potential φ can be written in the following form:

$$\varphi = \varphi_0 + \frac{59 \text{ mV}}{2 \times 2.3} \ln[\text{I}_2]$$

(φ_0 includes all the parameters which are held constant during the experiment.) The time dependence of the iodine concentration using the pseudo-first-order rate constant k_{14} is

$$[\text{I}_2] = [\text{I}_2]_0 \exp(-k_{14}t)$$

TABLE 1^a

no.	reaction		ref	for [H] = 1.2 × 10 ⁻³
Citri–Epstein Mechanism				
(R1)	HClO ₂ + I ⁻ + {H} → HOI + HOCl	{(4.6 + 31[H])[H]}/([H] + 3.3 × 10 ⁻³)	24	1.24
(R2)	HOI + I ⁻ + {H} → I ₂ + {H ₂ O}	5.0 × 10 ⁹ [H]/([H] + 2.0 × 10 ⁻³)	23	1.875 × 10 ⁹
(R3)	I ₂ + {H ₂ O} → HOI + I ⁻ + {H}	1.565 × 10 ⁻³ /([H] + 2.0 × 10 ⁻³)	26	4.89 × 10 ⁻¹
(R4)	HClO ₂ + HOI → HOCl + HIO ₂	1.683 × 10 ⁻⁵ [H]/(6.26 × 10 ⁻¹³ [H] + 2.0 × 10 ⁻¹⁵)	26	7.34 × 10 ⁶
(R5)	HOCl + I ⁻ → HOI + Cl ⁻	1.4 × 10 ⁸	23	1.4 × 10 ⁸
(R6)	HIO ₂ + I ⁻ + {H} → 2HOI	1.0 × 10 ⁶ [H]	23	1.2 × 10 ³
(R7)	2HOI → HIO ₂ + I ⁻ + {H}	25	23	25
(R8)	2HIO ₂ → IO ₃ ⁻ + HOI + {H}	3.0 × 10 ³	23	3.0 × 10 ³
(R9)	HIO ₂ + HOI → IO ₃ ⁻ + I ⁻ + {2H}	2.3 × 10 ²	23	2.3 × 10 ²
(R10)	HIO ₂ + HOCl → IO ₃ ⁻ + Cl ⁻ + {2H}	1.0 × 10 ³	23	1.0 × 10 ³
Lengyel–Rábai–Epstein Mechanism				
(R11)	ClO ₂ + I ⁻ + {H} → HClO ₂ + I	6.0 × 10 ³	2	6.0 × 10 ³
(R12)	2 I → I ₂	1.0 × 10 ⁹	2	1.0 × 10 ⁹
Experimentally Determined Rate Constants				
(R13)	→ I ₂	2.5 × 10 ⁻⁸	this work	2.5 × 10 ⁻⁸
(R14)	I ₂ + {CH ₃ COCH ₃ } → I ⁻ + {CH ₃ COCH ₂ I} + {H}	3.8 × 10 ⁻¹	this work	3.8 × 10 ⁻¹

^a { } indicates constant concentration.

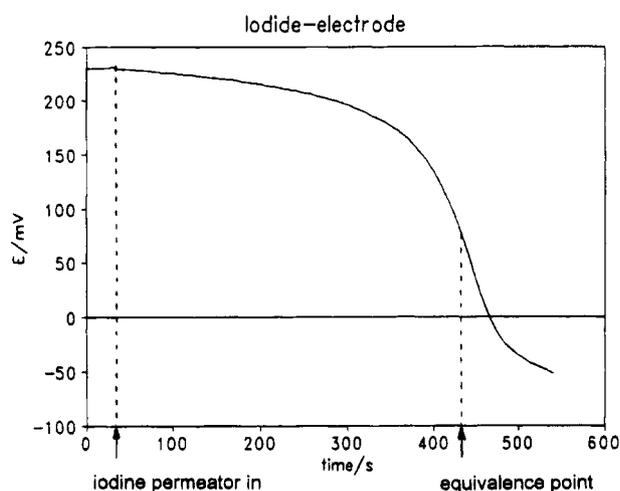


Figure 3. Determination of the I₂ inflow rate (k_{13}); titration curve. Initial conditions: $[Ag^+]_0 = 10^{-5}$ M, $[CH_2(COOH)_2]_0 = 0.1$ M, $[H_2SO_4] = 0.1$ M. Equivalence time = 430 - 30 = 400 s. $k_{13} = (10^{-5} M)/(400 s) = 2.5 \times 10^{-8} M s^{-1}$.

where

$$k_{14} = k'_{14}[CH_3COCH_3]$$

k'_{14} is the second-order rate constant for (R14). From these formulas

$$\varphi = \varphi'_0 - (12.8 \text{ mV})k_{14}t$$

where

$$\varphi'_0 = \varphi_0 + (12.8 \text{ mV}) \ln[I_2]_0$$

and

$$d\varphi/dt = (-12.8 \text{ mV})k_{14}$$

Model Calculations for the CIA Reaction. In the calculations no parameter fitting was attempted. All rate constants were used as they are given in the literature or found in our experiments (see Table 1). Integration was carried out using the LSODE routine for stiff systems of ordinary differential equations.³⁰ The results of the numerical simulations are depicted in Figure 5.

The CIA System with Two Permeators. The oscillations stop in both the system experiments and the model calculations when

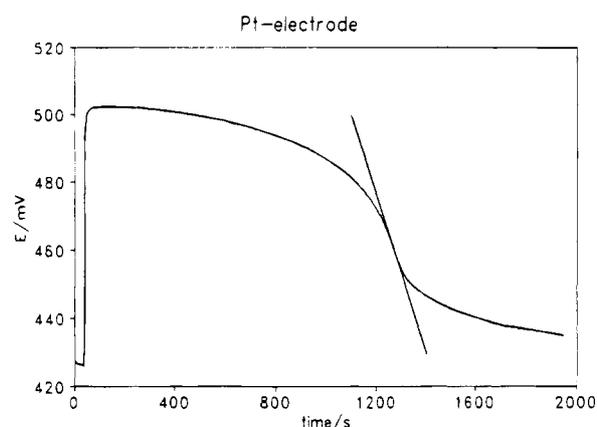


Figure 4. Determination of the pseudo-first-order rate constant k_{14} . Initial conditions: $[CH_3COCH_3]_{0,m} = (0.545 \text{ M})/20 = 0.0272 \text{ M}$, $[H^+]_0 = 1.2 \times 10^{-3} \text{ M}$, $[I^-]_0 = 2.4 \times 10^{-4} \text{ M}$, $[I_2]_0 = 10^{-5} \text{ M}$. Maximum slope: $|d\varphi/dt| = 0.245 \text{ mV/s}$. In this measurement the acetone concentration had to be chosen 20 times smaller than in the CIA system to slow the rate of the potential change. Thus $d\varphi/dt = (-12.8 \text{ mV}) \cdot k'_{14}[CH_3COCH_3]_m = (-12.8 \text{ mV}) \cdot (k_{14}/20)$. $k_{14} = 0.245 \times 20/12.8 = 0.38 \text{ s}^{-1}$.

chlorine dioxide is consumed. It was straightforward to assume that a chlorine dioxide source would maintain oscillations for a longer time. The experimental setup made it possible to insert an other permeator for chlorine dioxide. As the silicon rubber membrane was highly permeable to chlorine dioxide as well, this second permeator was the same type as that for iodine except that the permeator vessel was filled with a concentrated chlorine dioxide solution. It was found that the insertion of this second permeator considerably lengthened the duration of the oscillation. Figure 6 shows a part of such long-lived oscillations.

Conclusion

Comparing the experimentally found oscillations in the CIA reaction (Figure 2) with the results of the model calculations (Figure 5a,b), the qualitative agreement is remarkable. Both the period and the duration of the observed and calculated semibatch oscillations are rather close. On the other hand, the amplitudes are different. No attempts were made here to explain the absolute potential levels of the electrodes. Obviously, a careful calibration of the electrodes for all the possible electroactive species in the reaction mixture is needed together with some theoretical interpretation of the recorded mixed potentials.

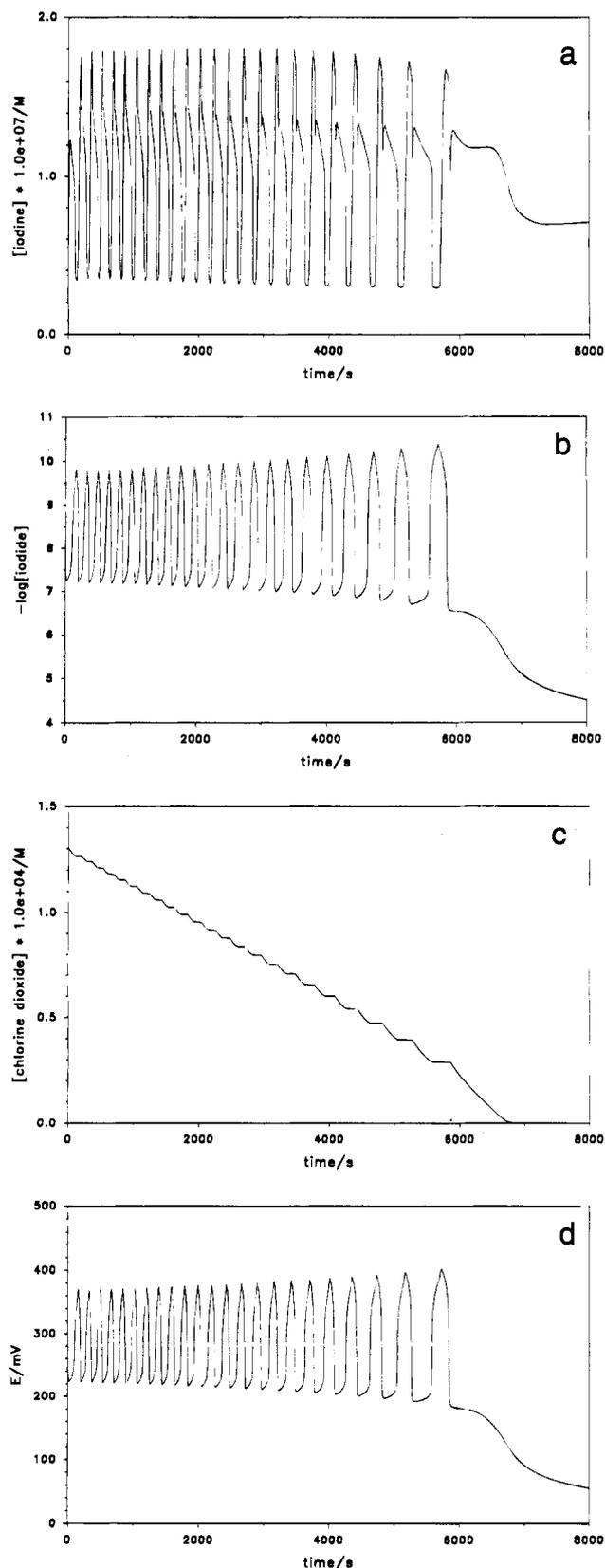


Figure 5. Results of numerical modeling with I₂ inflow only: (a) iodine concentration, (b) negative logarithm of the iodide concentration, (c) chlorine dioxide concentration vs time diagrams, (d) calculated redox potential oscillations on the platinum electrode. The calculations assume that the redox potential is determined by the iodine-iodide redox couple exclusively.

These electrochemical investigations, however, require a separate study, which is in progress.

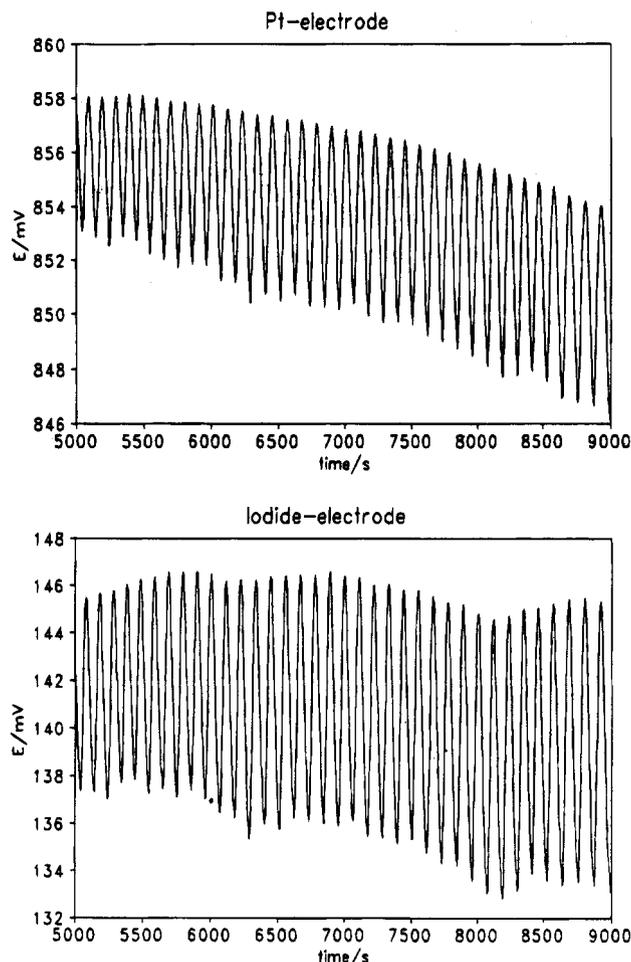


Figure 6. A 4000 s segment of the long-lived oscillations in the CIA system in the presence of two permeators (one for iodine and one for chlorine dioxide). The chlorine dioxide permeator contained about 1 mL of 0.065 M aqueous chlorine dioxide solution. Oscillations lasted more than 6 h.

Finally, the novel reactor design deserves a comment. An MSTR, the new semibatch reactor reported here, does not require pumps (like a CSTR) to keep the system far from equilibrium. It is the diffusional mass transport through selective membranes that maintains the nonequilibrium state of the system. This feature resembles the more complex transport processes associated with the metabolism of a living cell.

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