Realistic parameters for simple models of Bielousov-Zhabotynski reaction

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Abstract

We use the experimental results to estimate the values of parameters of a simple model of Bielousov-Zhabotynski reaction. The equations with fitted parameters correctly describe the period of oscillations for a large class of experimental conditions at which the reaction is performed.

1 Introduction

An increasing interest in applications of chemistry to information processing can be noticed in the recent years [1, 2, 3, 4]. This trend can be explained with quite obvious observation that chemical reactions are responsible for efficient information processing tasks performed by living organisms. It may be expected that studying biological computing can have an inspiring role and lead to new algorithms for complex tasks like optimization [5] or image recognition. A typical nerve system is build of non-linear elements (cells) that are linked together to form a network. An excitation of one cell can influence all those it is linked with. Experimental studies on real nerve cells are difficult and costly. However recently chemists focused attention on its cheap

substitute: droplets filled with reagents of reaction exhibiting a complex, non-linear dynamics that are separated by surrounding, unmisable liquid. Droplets containing the water solution of reagents of Bielousov-Zhabotynski reaction surrounded by hydrocarbons are the most common version of such system [6]. The presence of surfactants [6, **?**] or lipids [7] covers BZ-solution with a monolayer. The presence of monolayer mechanically stabilizes droplets so their structures remain unchanged for hours. For information processing applications the fact that droplets interact via diffusion of reagents through the surrounding hydrocarbons is equally important. These features combined with a long time within which the BZ-medium inside droplets remain "life" makes a BZ-droplet system an interesting candidate to study information processing phenomena.

It can be shown that in information processing applications the structure of medium defined as the geometrical distribution of regions characterized by different chemical dynamics plays equally important role as the properties of chemical reactions involved. For example by arranging the droplets in a specific manner we can obtain structures operating as basic logic gates [8, 9]. The theoretical studies on interesting signal processing structures are usually based on numerical simulations with simplified models of chemical processes like for example the Oregonator model. The parameters used in calculations are selected to give a correct qualitative description of the system, but it is qiute hard to translate them into real physical conditions and suggest experiments. In this paper we consider two simple models of Bielousov-Zhabotynski reaction and fix they parameters to obtain the best agreement with a large class of experimental results. The proposed models take the experimental conditions as input parameters, so they can be directly used to estimate the concentrations of reagents at which the required effects should appear.

2 Simple models for oscillatory evolution

Our experiments with the Bielousov-Zhabotynski reaction in lipid covered droplets [7] have demonstrated that if the droplet is not too small (its diameter is of the order of 1 mm) then the presence of lipid layer has a minor influence on the reactions. The period of oscillations in droplets of that size are the same as in a test tube with well stirred solution characterized by the same composition of reagents. Therefore, we can describe the time evolution of reagents in droplets with a simple model of Bielousov-Zhabotynski reaction that does not take into account the reactions with lipids. A simple, few variable model that can be derived form the Field-Kores-Noyes(FKN) reac-

tion scheme []. After some simplifications [**?**, **?**] the FKN reaction scheme can be reduced to the following kinetic equations:

$$\frac{\partial X}{\partial t} = k_1 h_0 AX - 2k_4 h_0 X^2 - k_5 h_0 XY + k_7 h_0 AY \tag{1}$$

$$\frac{\partial Y}{\partial t} = q\frac{k_8 k_9}{k_{-8}}\frac{B}{h_0}\frac{Z}{(C-Z)} - k_5 h_0 XY - k_7 h_0 AY + k_{13} B \tag{2}$$

$$\frac{\partial Z}{\partial t} = 2k_1 h_0 AX - \frac{k_8 k_9}{k_{-8}}\frac{B}{h_0}\frac{Z}{(C-Z)} \tag{3}$$

The model variables X, Y and Z denote concentrations of $HBrO_2$,Br^- and $Fe(phen)_3^{3+}$ respectively. In Eqs.(1-3) the symbols k_{+-i} represent the rate constants of the corresponding reaction within the FKN reaction scheme. h_0 is the Hammet acidity function of the solution and for the concentrations of sulfuric acid used in our experiments it can be approximated as 1.3 times higher than the concentration of H_2S0_4. The capital letters A, B and C denote the concentrations $HBrO_3$, bromomalonic acid $CHBr(COOH)_2$ and the total concentration of the catalyst ($C = [Fe(phen)_3^{2+}] + [Fe(phen)_3^{3+}]$). We assume that the values A, B and C remain constant during the evolution.

However, setting an experiment we know the total concentration of the catalyst C but we do not know the concentrations of $HBrO_3$ nor the concentration of bromomalonic acid. To link these concentrations with the initial solution of reagents We assume that the concentration of $HBrO_3$ is proportional to the concentration of $NaBrO_3$ used in experiment:

$$A = [HBrO_3] = \eta[NaBrO_3] = \eta N$$

and that the concentration of $CHBr(COOH)_2$ is proportional to the product of $CH_2(COOH)_2$ and KBr:

$$B = [CHBr(COOH)_2] = \xi[CH_2(COOH)_2] * [KBr] = \xi M * K$$

In Eqs.(2,2) symbols K, M and N denote concentrations of KBr, $CH_2(COOH)_2$ and $NaBrO_3$ respectively. It is convenient to consider K, M and N as parameters of the model because these reagents are used in our experiments.

Introducing the scaled concentration of the oxidized catalyst:

$$z = Z/C$$

and the scaled concentration of X defined as:

$$x = 2k_1 \eta X$$

one transforms Eqs.(3) into:

$$\frac{\partial z}{\partial t} = \frac{h_0 N}{C} x - \alpha \frac{K * M}{C h_0} \frac{z}{(1-z)} \tag{4}$$

where

$$\alpha = \frac{k_8 k_9}{k_{-8}} \xi$$

If we introduce the scaled concentration of Y in the form:

$$y = \frac{Y}{k_{13} \xi}$$

then Eqs.(2) transforms into:

$$\frac{\partial y}{\partial t} = q\beta \frac{M * K}{h_0} \frac{z}{1-z} - \gamma h_0 x y - \gamma \mu h_0 N y + M * K \tag{5}$$

where

$$\gamma = \frac{k_5}{2 k_1 \eta}$$

$$\mu = \frac{k_7 \eta}{\gamma} = \frac{2 k_1 k_7 \eta^2}{k_5}$$

$$\beta = \frac{k_8 k_9 k_{13}}{k_{-8}}$$

Finally within such scalling Eqs.(1) can be written as:

$$\frac{\partial x}{\partial t} = \epsilon_1 h_0 N x - \epsilon_2 h_0 x^2 - 2 \frac{\alpha \gamma \epsilon_1}{\beta} h_0 x y + 2 \frac{\alpha \gamma \epsilon_1 \mu}{\beta} h_0 N y \tag{6}$$

where

$$\epsilon_1 = k_1 \eta$$

$$\epsilon_2 = \frac{k_4}{\epsilon_1} = \frac{k_4}{k_1 \eta}$$

Let us notice that all parameters of the model: $\alpha, \beta, \gamma, \epsilon_1, \epsilon_2, \mu$ and q depend on the rate constant and they are not related to concentrations of any considered reagents. Therefore, the model based on equations (Eqs.(6),Eqs.(5),Eqs.(4)) can be directly used to describe the time evolution of solution of reagents prepared with known concentrations of H_2SO_4, KBr, $CH_2(COOH)_2$, $NaBrO_3$ and the catalyst. We think it makes it superior to the Rovinski-Zhabotynski model of BZ-reaction [**?**] where the parameter has to be calculated separately for each experimental case.

The system based on equations (Eqs.(6),Eqs.(5),Eqs.(4)) can be made simpler if we assume that the relaxation of y is fast and the stationary value of y is immediately approached. Calculating the steady value of y from Eq.(5) and substituting it to Eq.(6) we obtain:

$$\frac{\partial x}{\partial t} = \epsilon_1 h_0 N x - \epsilon_2 h_0 x^2 - 2\alpha\epsilon_1 M * K(\frac{1}{\beta} + q\frac{1}{h_0}\frac{z}{1-z})\frac{x-\mu N}{x+\mu N} \qquad (7)$$

The set of equations: (Eqs.(7),Eqs.(4)) with parameters $\alpha, \beta, \epsilon_1, \epsilon_2, \mu$ and q makes a two variable model describing the Bielousov-Zhabotynski reaction in lipid covered droplets.

3 Experimental results and parameter fitting

In experiments we measured the period of oscillations in a small droplet of BZ-reagents surrounded covered by phospholipid layer. The medium used was composed of two unmiscible phases. One is the solution of a phospholipid L-α-phosphatidylcholine (Soy-20% - Avanti Polar Lipids, Inc.) in decane, prepared by dissolving 1 g of lipids in 50 ml of decane. The second phase is the aqueous solution of reagents of ferroin-catalyzed BZ reaction corresponding to an oscillating regime. It is prepared as follows: water, sulfuric acid, sodium bromate, malonic acid, potassium bromide and ferroin. All the reagents were analytical grade used without further purification. We performed experiments for over 60 different compositions of reagents. In ferroin catalyzed BZ reaction changes in concentration of reagents are indicated by changes in color: the solution is blue for a high concentration of oxidized catalyst and red when the catalyst is reduced. Therefore, information on the time evolution and period can obtained from visual observation of the system. Droplets were observed with a digital video camera, next the film was digitally processed and period of oscillations was calculated.

The model parameters have been obtained from the experimental results for period as a function of compositions of reagents. We used optimization procedure that minimized differences between the observed period and the one calculated from model equations for all set of experimental conditions. For the model based on (Eqs.(6),Eqs.(5),Eqs.(4)) the best agreement was obtained for $\alpha = 1.1 * 10^{-4}$, $\beta = 200.$, $\gamma = 6000.$, $\epsilon_1 = 4300.$, $\epsilon_2 = 8800.$, $\mu = 2.5 * 10^{-5}$ and $q = 0.6$. The periods obtained form three-equation model with such parameters are shown by the solid line in Figure 2 and compared with the experimental results (open cycles). It can be seen that the this model gives quite accurate description of the trends in period changes as a function of concentration of one of the reagents.

Using the parametres of the three equation model we can verify if the equation on stationarity of y variable is correct. Figure 1 shows one particular case. The solid line shows time evolution predicted by three-variable model whereas the dashed one is calculated from x and z assuming that it corresponds to the steady state of Eqs(5). It can be seen that for almost all period the real value of y is by 10excitation the agreement fails and the numbers differ by an order of magnitude. Therefore, it is hard to believe that the parameters of three-variable model can be directly used in the two-variable model. Having this in mind we treated the model based on (Eqs.(7),Eqs.(4)) independently and performed optimization of its parameters for the same set of experimental results. For two-variable model the optimization procedure gives the best fit for: $\alpha = 2.6 * 10^{-4}$, $\beta = 200.$, $\epsilon_1 = 4000.$, $\epsilon_2 = 5800.$, $\mu = 2.1 * 10^{-5}$ and $q = 0.88$. The periods calculated for such parameters are shown by the dashed line in Figure 2. The agreement is poorer than that for three-variable model, but still most of the trends in period changes are correctly represented.

4 Conclusions

We think, we were able to show the vales of parameters for whic a relativel simple model gives quite nice description of periods observed in BZ-reaction at a wide class of experimental conditions. The model can be used to predict experimental conditions for the other, required types of behaviour. For example the two-variable model predict excitability when $C = 0.0017$, sodium bromate concentration is 0.45, the concentration of sulfuric acid is reduced to 0.02 and the product of concentrations of malonic acid and potasium bromide is increased to 0.084.

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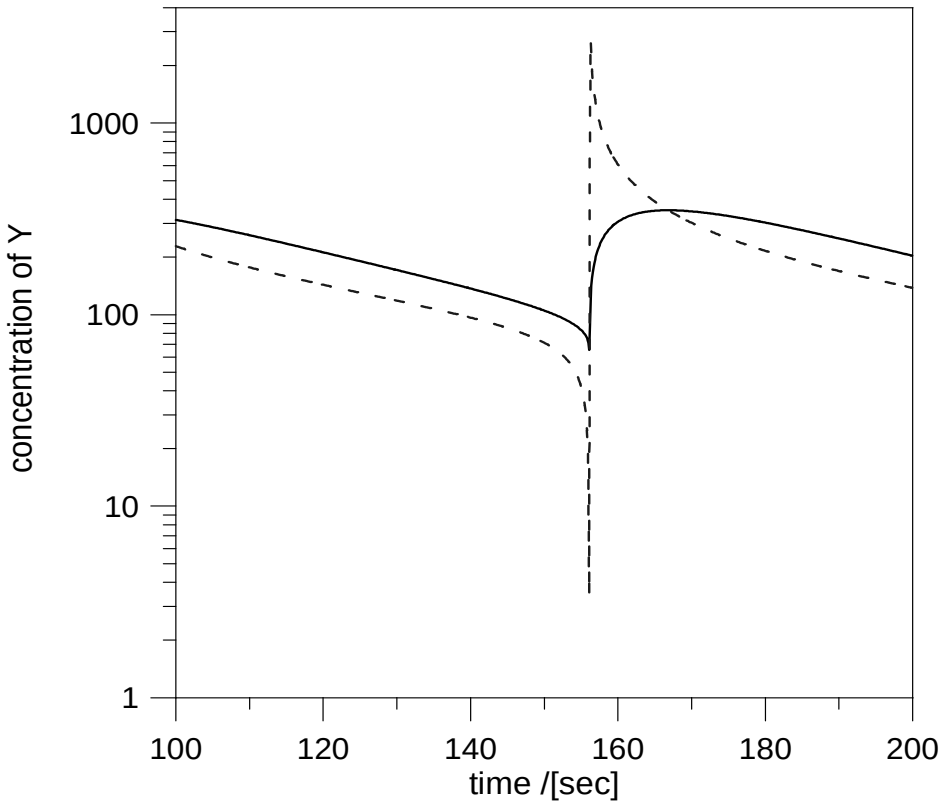

Figure 1: The time evolution of y within once cycle. The solid line represents the three variable model, the dashed one results of two-variable model. Calculations were performed for the following conditions $[H_2SO_4] = 0.30$, $[NaBrO_3] = 0.45$, $[CH_2(COOH)_2] = 0.35$, $[KBr] = 0.06$ and $C = 0.0017$.

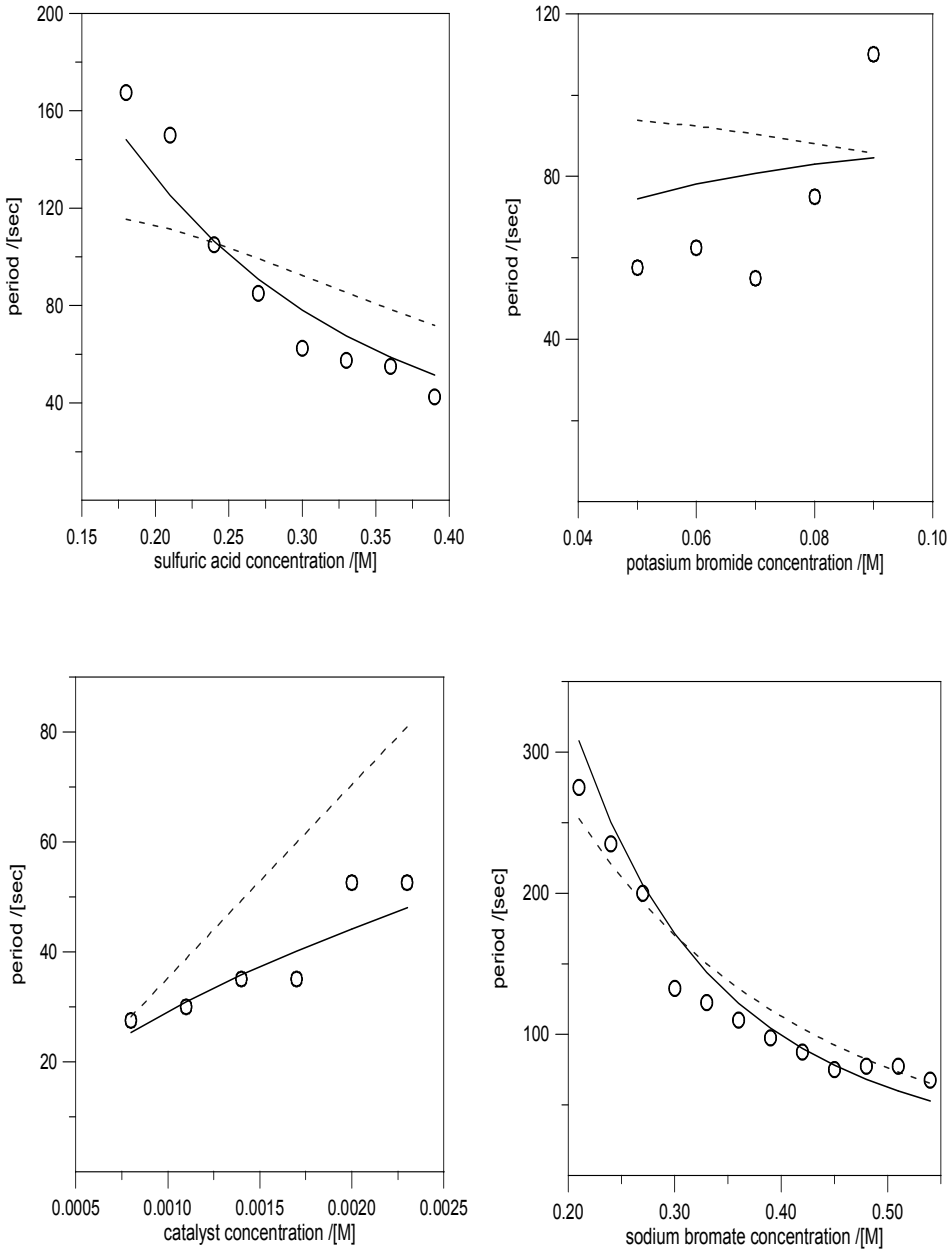

Figure 2: Period as a function of concentration of different reagents. Crosses correspond to experimental results, the solid line has been calculated from the Rovinsky-Zhabotynski model with parameters given in the text. The figures clockwise starting form the upper left corner were calculated for the following conditions: A - $[NaBrO_3] = 0.45$, $[CH_2(COOH)_2] = 0.35$, $[KBr] = 0.06$ and $C = 0.0017$; B - $[H_2SO_4] = 0.30$, $[NaBrO_3] = 0.45$, $[CH_2(COOH)_2] = 0.35$, and $C = 0.0017$; C - $[H_2SO_4] = 0.45$, $[NaBrO_3] = 0.45$, $[CH_2(COOH)_2] = 0.35$, and $[KBr] = 0.06$; D - $[H_2SO_4] = 0.30$, $[CH_2(COOH)_2] = 0.35$, $[KBr] = 0.06$ and $C = 0.0017$.

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