

## Analysis of diffusivity of the oscillating reaction components in a microreactor system

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original scientific paper  
DOI: 10.17508/CJFST.2017.9.1.06

### Summary

When performing oscillating reactions, periodical changes in the concentrations of reactants, intermediaries, and products take place. Due to the mentioned periodical changes of the concentrations, the information about the diffusivity of the components included into oscillating reactions is very important for the control of the oscillating reactions. Non-linear dynamics makes oscillating reactions very interesting for analysis in different reactor systems. In this paper, the analysis of diffusivity of the oscillating reaction components was performed in a microreactor, with the aim of identifying the limiting component. The geometry of the microreactor microchannel and a well defined flow profile ensure optimal conditions for the diffusion phenomena analysis, because diffusion profiles in a microreactor depend only on the residence time. In this paper, the analysis of diffusivity of the oscillating reaction components was performed in a microreactor equipped with 2 Y-shape inlets and 2 Y-shape outlets, with active volume of  $V = 4 \mu\text{L}$  at different residence times.

**Keywords:** diffusivity, oscillating reaction components, microreactor

### Introduction

Microtechnology has a wide area of application; from electronics, medical technology, and fuel production, through biotechnology, chemical industry, and environment protection, to process safety. The size of the process space at the scale of only a few micrometers has numerous advantages when compared to a classical reactor; small amounts of chemicals are needed, high rate of heat and mass transfer can be achieved, reactions with toxic, flammable, and explosive reactants can be safely performed, etc. (Plazl and Lakner, 2010). Due to their characteristics, microreactors have become interesting in the field of flow chemistry. In flow chemistry, the reagents are continuously pumped through the reactor and products are continuously collected at the reactor outflow. Mixing of the components in a reactor relies on two phenomena, diffusion and convection (convection in the flow direction and diffusion in three dimensions) (Némethné-Sóvágo and Benke, 2014). For most chemical and biochemical processes, especially those taking place in multiphase systems, diffusion presents a limiting step (Häusler et al., 2012). By decreasing the reactor size, the distance that molecules have to cover also decreases, and consequently diffusion times become significantly shorter.

Low values of Reynolds numbers ( $Re < 100$ ) are characteristic for microreactor microchannels, which indicates that laminar flow is dominant and that mass transfer is determined by diffusion (Plazl and Lakner,

2010). Diffusion phenomena are described by Fick's Law that correlates the concentration time change and the product of diffusion coefficient, and the concentration gradient. Small molecules, characterised by higher values of diffusion coefficients, can diffuse and be distributed between phases even at short residence times. On the other hand, larger molecules, like enzymes and whole cells, diffuse very slowly and usually remain in the phase in which they are being introduced into the microsystem. As the consequence of the concentration gradients created by the flow of two fluids in opposite directions, a mixture of fluids with different concentrations, dependent on the position, can be formed. The application of the diffusivity in microreactors can be divided into: (i) extraction of cells from suspensions, (iii) mass transfer with stable concentration gradients, and (iii) effective mixing of fluids to intensify solvent diffusion (Brobana et al., 2011).

In this paper, diffusion phenomena of the oscillating reaction components were analysed in an aqueous two phase system, in a microreactor. In oscillating chemical reactions, the concentrations of the reactants and products change with time, in a periodical or quasi-periodical manner. Chemical oscillators exhibit chaotic behaviour, in which concentrations of products and the course of a reaction depend on the initial reaction conditions. Oscillating reactions are very common in biological systems. The exact mechanisms of oscillating reactions are elusive and difficult to obtain. The chemical equations and mechanisms based on stoichiometry

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describe only the overall reactions; they do not specify the molecular transformations that take place between colliding molecules (Zhuravlev and Trainin, 1990).

The aim of this paper was to analyse the diffusivities of the oscillating reaction components in a microreactor, in order to define the limiting component for performing oscillating reactions in a continuously operated microreactor.

## Materials and methods

### Chemicals

Potassium iodate ( $\text{KIO}_3$ ), malonic acid ( $\text{C}_3\text{H}_4\text{O}_4$ ), manganese sulphate monohydrate ( $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ ), starch ( $(\text{C}_6\text{H}_{12}\text{O}_6)_n$ ), and ammonium metavanadate ( $\text{NH}_4\text{VO}_3$ ) were purchased from Fisher Chemicals (Great Britain). Sulphuric acid ( $\text{H}_2\text{SO}_4$ ) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) were purchased from Carlo Erba (Italy), while potassium bromide ( $\text{KBr}$ ) and potassium bromate ( $\text{KBrO}_3$ ) were purchased from Kemika (Croatia).

### Determination of concentrations

Concentrations of all of the components except hydrogen peroxide were determined using a conductometer (Seven Compact™, Mettler Toledo, Canada). Concentration of the hydrogen peroxide was determined by using the ammonium metavanadate method (Galil et al., 2007).

### Diffusivity analysis in a microreactor

All experiments were performed in a microreactor system. A microchip with borosilicate tubular glass microchannels (length: width: height = 332 mm: 250  $\mu\text{m}$ : 50  $\mu\text{m}$ , with internal volume of 4  $\mu\text{L}$ ), equipped with two “Y”-shaped inflows and two “Y”-shaped outflows was used. Two syringe pumps (NE-1000 Syringe Pump, New Era Pump Systems, USA) were used for pumping the liquids (one pump for the solution of the oscillating reaction component, and the other for the distilled water – aqueous two phase system). The microreactor chip was connected to the pumps with a fused silica connection (375  $\mu\text{m}$  O.D., 150  $\mu\text{m}$  I.D., Micronit Microfluidics B.V., Netherlands). The fluid flow in a microreactor was observed using a microscope (Motic B1-220A, binocular Weltzar, Germany) at the magnification of 40x (eyepiece magnification = 10x; objective magnification = 4x). Samples were gathered separately at the outflows from the microreactor and concentrations were determined as described. Experiments were performed at different total flow rates:  $q = 2, 3, 5, 10, 20, 30, 50, 60, 70, 80, 90, 100, 150, 200, 250, 300, 350$ , and  $400 \mu\text{L min}^{-1}$ .

All experiments were performed in triplicates and no statistical difference between the data was observed.

### The velocity profile and the mathematical model of the mass transfer in a microreactor

According to Žnidaršič-Plazl and Plazl (2007), the velocity profile in the analyzed microreactor was described by Poiseuille-type, taking into account the steady-state flow of the aqueous phase and neglecting the compressibility and gravitational force (Eq. 1):

$$0 = -\frac{\Delta p}{L} + \frac{\eta_w}{W} \cdot \left[ \frac{\partial^2 v}{\partial \psi^2} + \frac{\partial^2 v}{\partial \omega^2} \right]$$

$$\begin{aligned} v(\pm 1, \omega) &= 0 & 0 \leq \omega \leq \frac{H}{W} \\ v(\psi, 0) &= 0 & -1 \leq \psi \leq 1 \\ v\left(\psi, \frac{H}{W}\right) &= 0 & -1 \leq \psi \leq 1 \end{aligned} \quad (1)$$

where dimensionless variables  $\psi$  and  $\omega$  are defined as  $\psi = y/W$  and  $\omega = z/W$ ,  $y$  and  $z$  are coordinated in the direction of the channel width and height.  $\eta_w$  is the dynamic viscosity of water and  $\Delta p/L$  is the constant pressure gradient along the length of the microchannel.

The reactor model was described with a 2D model, including the convection in the flow direction ( $x$ ) and diffusion in two directions ( $x$  and  $y$ ) (Tišma et al., 2009) (Eq.2). The model is based on the assumptions that the flow in the reactor is laminar, and that both phases have the same viscosity and occupy the same fraction of the channel (Tišma et al., 2009).

$$v \frac{\partial c}{\partial \xi} = \frac{D_A}{W} \left[ \frac{\partial^2 c}{\partial \xi^2} + \frac{\partial^2 c}{\partial \psi^2} \right]$$

$$\begin{aligned} c(0, \psi) &= c_i & -1 \leq \psi < 0 \\ c(0, \psi) &= 0 & 0 < \psi \leq 1 \\ \frac{\partial c}{\partial \xi} \left( \frac{L}{W}, \psi \right) &= 0 & -1 \leq \psi \leq 1 \\ \frac{\partial c}{\partial \xi} (\xi, \pm 1) &= 0 & 0 \leq \xi \leq \frac{L}{W} \end{aligned} \quad (2)$$

Here  $v$  represents linear velocity,  $\xi$  and  $\psi$  represent independent dimensionless variables ( $\xi = x/W$ ,  $\psi = y/W$ ),  $x$  and  $y$  are coordinated in the length ( $L$ ) and microchannel width ( $2W$ ). The mathematical models for the velocity profile and diffusivity of the analysed components of the oscillating reactions in the microreactor were solved by using a finite difference method algorithm on an equidistant grid developed in WR Mathematica 10.0.

**Table 1.** Effective diffusivity coefficients ( $D_{ef}$ ) for the eight analysed components of oscillating reactions in an aqueous medium

Component	$D_{ef}$ [ $\text{m}^2\text{s}^{-1}$ ]	Reference
potassium iodated	$4.500 \cdot 10^{-9}$	(Adekunle et al., 2012)
malonic acid	$8.020 \cdot 10^{-10}$	(Teixeira et al., 1994)
hydrogen peroxide	$8.796 \cdot 10^{-10}$	(van Store-Biezen et al., 1993)
starch	$9.900 \cdot 10^{-13}$	(Juna et al., 2011)
manganese sulphate	$7.350 \cdot 10^{-10}$	(Emanul and Olander, 1963)
sulphuric acid	$1.962 \cdot 10^{-9}$	(Leaist, 1984)
potassium bromide	$1.975 \cdot 10^{-9}$	(Flury et al., 2002)
potassium bromate	$1.551 \cdot 10^{-9}$	(Katsounaros et al., 2010)

### Diffusivity times

Taking into account the diameter of the microchannels of the used microreactor and the effective diffusivity data of the analyzed components available in the literature (Table 1), diffusivity times were calculated according to Eq. 3.

$$t = \frac{d^2}{D_{ef}} \quad (3)$$

A comparison of the diffusivity times between a classical macroreactor ( $d = 2.0 \cdot 10^0$  m) and the used microreactor ( $2.5 \cdot 10^{-4}$  m) was made.

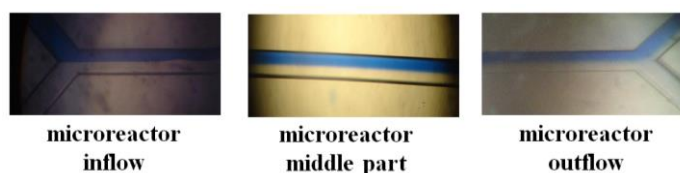
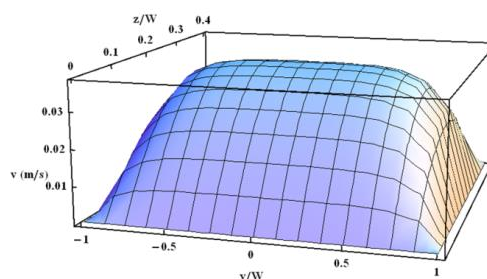
### Results and discussion

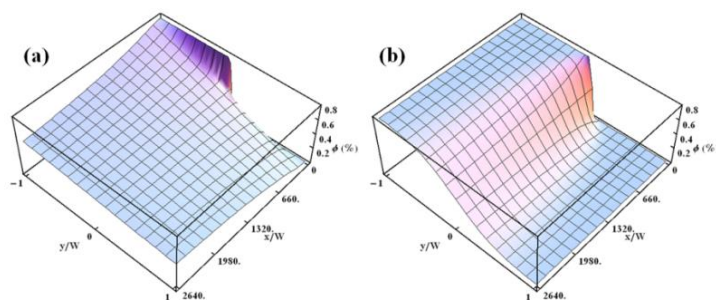
In order to confirm the laminar and parallel flow, two aqueous phases were introduced into a microreactor and flow profiles were observed under the microscope. In order to distinguish the two aqueous phases, one was stained blue while the other was kept colourless. The

photography of the flow profile at the total flow rate of  $q = 50 \mu\text{L min}^{-1}$  is given in Fig. 1.

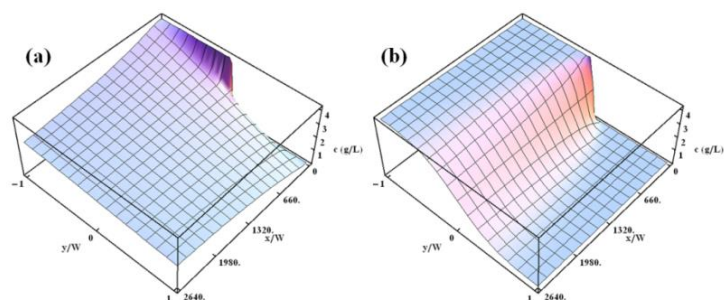
It can be noticed that the flow was laminar and parallel, and that the interface was in the middle of the channel. The obtained flow profile confirmed the applicability of the used mathematical model for the description of the concentration profiles in the analysed microreactor geometry. The velocity profile in the microreactor was calculated using Eq. 1. The simulation of the mathematical model of the velocity profile at the total flow rate of  $q = 50 \mu\text{L min}^{-1}$ , immediately after entering into a microreactor, is presented in Fig. 2.

The diffusivity profiles for three of the eight components of oscillating reactions (hydrogen peroxide, malonic acid, manganese (II) sulphate, potassium iodate, starch, sulphuric acid, potassium bromide and potassium bromate) in the microreactor, obtained by solving the partial differential equations for the total flow rates of  $q = 2 \mu\text{L min}^{-1}$  and  $q = 200 \mu\text{L min}^{-1}$  are given in Fig. 3-5.

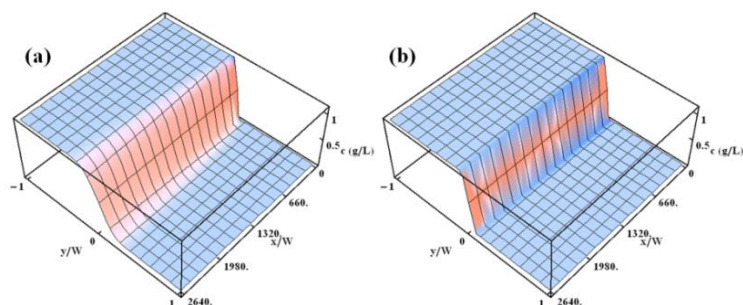
**Fig. 1.** Photography of the flow pattern of two aqueous phases in a microreactor at total flow rate of  $q = 50 \mu\text{L min}^{-1}$ **Fig. 2.** The simulation of the mathematical model of a velocity profile at the total flow rate of  $q = 50 \mu\text{L min}^{-1}$  (immediately after the entering into a microreactor)



**Fig. 3.** The diffusivity profile for hydrogen peroxide in a microreactor at two different total flow rates  
(a)  $q = 2 \mu\text{L min}^{-1}$  and (b)  $q = 200 \mu\text{L min}^{-1}$



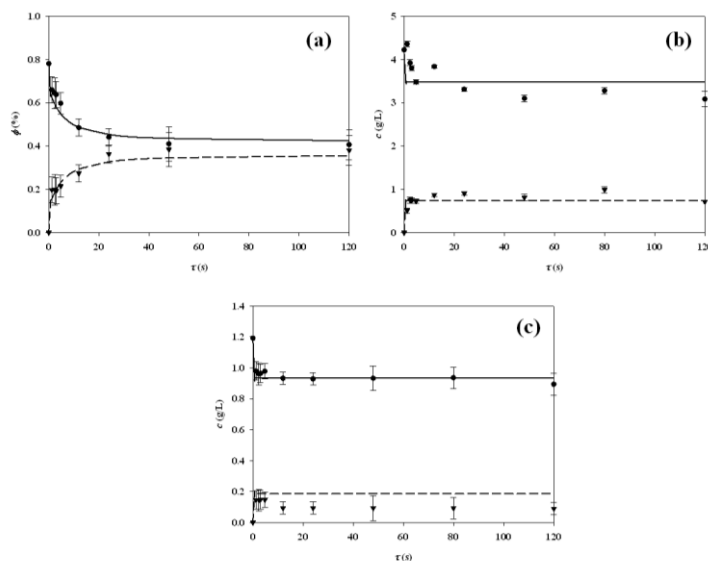
**Fig. 4.** The diffusivity profile for manganese (II) sulphate in a microreactor at two different total flow rates  
(a)  $q = 2 \mu\text{L min}^{-1}$  and (b)  $q = 200 \mu\text{L min}^{-1}$



**Fig. 5.** The diffusivity profile for starch in a microreactor at two different total flow rates  
(a)  $q = 2 \mu\text{L min}^{-1}$  and (b)  $q = 200 \mu\text{L min}^{-1}$

By analyzing the obtained diffusivity profiles for the components of the oscillating reactions in a microreactor, it can be observed that small molecules, like hydrogen peroxide and manganese (II) sulphate, diffuse very quickly from one aqueous phase to another. Diffusion takes place even at the highest analysed total flow rate of  $q = 200 \mu\text{L min}^{-1}$  at the microreactor outflow. Results have also shown that hydrogen peroxide and manganese (II) sulphate distributed almost evenly in both aqueous phases at the microreactor outflow, at the total flow rate of  $q = 2 \mu\text{L min}^{-1}$ .

Simulations of the diffusion model for starch show that there is no distribution of the starch molecules between the two phases through the microchannel length. Results show that even at the lowest analysed total flow rate, most of the analysed molecules stay in one phase. The obtained results indicate that starch would be the limiting component for the oscillating reactions in a microreactor. Based on the obtained results, a future experiment with oscillating reactions (especially Briggs-Rauscher reaction; BR reaction) in micro scale can be planned by taking into account that effective mixing should be ensured.



**Fig. 6.** The comparison between experimental data and simulation results for the diffusivity profiles of (a) hydrogen peroxide, (b) manganese sulphate, and (c) starch in a microreactor at different residence times ((●) experimental data for extract phase, (—) mathematical model for extract phase, (▼) experimental data for raffinate phase, (---) mathematical model for raffinate phase)

**Table 2.** Diffusion times for the eight analysed components of oscillating reactions in a macro- and microreactor

Component	Diffusion time (s)	
	Macroreactor	Microreactor
potassium iodated	$8.88 \cdot 10^8$	13.88
malonic acid	$4.98 \cdot 10^9$	77.93
hydrogen peroxide	$4.54 \cdot 10^9$	71.05
starch	$4.04 \cdot 10^{12}$	$6.31 \cdot 10^4$
manganese sulphate	$5.44 \cdot 10^9$	85.03
sulphuric acid	$2.08 \cdot 10^9$	32.55
potassium bromide	$2.02 \cdot 10^9$	31.64
potassium bromate	$2.58 \cdot 10^9$	40.29

The comparison between experimental data and simulation results for the concentration profile of hydrogen peroxide, manganese sulphate, and starch in two phases, in a microreactor at different residence times is presented in Fig. 6. The diffusivity of the hydrogen peroxide was analysed for residence time in the range from  $\tau = 0$  s to  $\tau = 140$  s. As presented in the Fig. 6a, it can be noticed that at residence times longer than  $\tau = 50$  s, the equilibrium is reached between concentrations in both phases. By analyzing the mean square deviation, it can be concluded that the model describes the extract phase ( $R^2 = 0.992$ ) more precisely than the raffinate phase ( $R^2 = 0.343$ ). Diffusivity of the manganese sulphate was also analysed for residence times in the range from  $\tau = 0$  s to  $\tau = 140$  s. The results presented in Fig. 6b show that the equilibrium between concentrations in both aqueous phases is reached at residence times longer than  $\tau = 70$  s. The mean square deviation also shows that the model describes concentrations in the extract phase ( $R^2 = 0.796$ ) more

precisely than concentrations in the raffinate phase ( $R^2 = 0.491$ ). Opposite to previously described concentration profiles, the model simulation results show that starch molecules (Fig. 6c) stay at the extract phase for all analysed residence times. This can be explained by the fact that starch has significantly higher molecular mass compared to other analysed molecules and consequently the diffusion rate is small. The used geometry of the microreactor was not suitable for experiments with starch (reactor was too short). The possible solution would be to use a microreactor equipped with micromixers, a longer period of pre-treatment (solubility of the starch), reduced concentration of starch used in the oscillating reaction, etc. In case of starch, it can also be noticed that there is a significant deviation between experimental data and model simulation results ( $R^2$  (extract phase) = 0.232,  $R^2$  (raffinate phase) = 0.032).

The diffusion time, defined as a ratio of the square of the reactor diameter and the effective diffusivity coefficient

of a specific component, is a very important parameter in the process industry. The list of the calculated diffusion times for all analysed oscillating reaction components in a macro- and micro-reactor are presented in Table 2.

By analysing the calculated values of diffusion times given in Table 2, it can be noticed that diffusion times are significantly shorter in microreactors, compared to classical macroreactors (approximately eight fold). Based on the obtained results, it can be concluded that microreactors are a good alternative to classical macroreactors for performing oscillating reactions in very short residence times. The calculated values of diffusion times also indicate that starch would be a limiting component for performing oscillating reactions in a microreactor. The calculated value of the diffusion time of starch is three times higher than for the other components, indicating that the selected microreactor geometry is not suitable for the diffusion of starch from one phase into another. To ensure a more effective mass transfer, it would be necessary to provide for the mixing of phases, in order to enable fast contact between starch and other components of oscillating reactions. Microreactors equipped with micromixers could be a possible solution.

## Conclusions

The analysis of diffusivities and diffusion times of the oscillating reaction components (hydrogen peroxide, malonic acid, manganese (II) sulphate, potassium iodate, starch, sulphuric acid, potassium bromide, and potassium bromate) showed that microreactors are suitable for performing oscillating reactions and that starch presents a limiting component. The concentration profiles of the oscillating reaction components can be described using a 2D mathematical model of mass transfer in a microreactor.

## Acknowledgements

This study is a contribution to the project „Application of Microreactors in the Analysis of Antioxidant Activity of Medicinal Plants (MICRO-AA)“, project number HR.3.2.01-0069, which is funded by the European Social Fund (ESF) through the Human Resources Development program.

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**Received:** November 17, 2016

**Accepted:** December 14, 2017