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Double-Diffusive Convection in the Continuous Flow Microreactors

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Abstract. In this paper, the mixing process of two solutions of inorganic salts in a continuous flow channel with Y-type micromixer is investigated. Due to different diffusivity rates of solutes the double-diffusion convection develops in the channel. To visualize convective flows and the distribution of mixing substances the shear interferometer technique and a fluorescent dye are used. The latter makes it possible to quantify the mixing degree. The mixing extent for different volume flow rates is calculated. The comparison of convection and pure diffusion mechanisms of mixing is provided.

1. Introduction

Continuous flow reactors find an application in various chemical engineering, pharmaceutical, and biological technological processes (see detailed literature review in [1]). In continuous flow reactors, the reactants are permanently delivered through inlets into a reaction zone where they mix and react completely with each other forming the reaction product at the outlet of the zone. High productivity, uniform, and stable conditions, simple control in consumption of reagents and energy, and a possibility to increase in output by elements' replication are the main but not exhaustive advantages with respect to the traditional batch-reactors. In connection with the needs of pharmaceutical production in flexible and reconfigurable flow systems with low product yield, microfluidic systems with reactor zone size in the millimeter and submillimeter range have become widespread in recent years [2-7]. The transition to the micro-scale led to the problem of reagents mixing. Due to the small transverse dimension of the reaction zone, the flow is laminar inside it and the transverse mixing of the reagents becomes possible solely due to diffusion. Because of the low rate of the diffusion processes, this needs rather elongated reaction zones to provide complete mixing which results in a significant increase in the time required to complete the reaction.

To reduce the reaction time various mixing systems were proposed. There are two main types of mixing systems: active and passive. The former requires the supply of energy from the outside in the form of mechanical energy, heat [8], or the energy of electric or magnetic fields [9]. The use of this type of mixing system is usually limited in microreactors due to the small size of the reaction zone or the immunity of the reacting substances to electromagnetic influences. Passive mixing systems use the internal energy of the flow. In addition to the above-mentioned diffusion, convection is an effective way to mix the reagents. The most widespread way consists of creating a complex geometry of the reaction zone to form chaotic flows that stretch, recombine, and fold the mixing interface between streams providing thus the media homogenization, resulting in a considerable increase in the product output [10-16]. The disadvantage of this type of mixing system is significant pressure has to be applied to pump liquid through geometrically complex zones, involving higher energy costs. A more attractive way is to create conditions for the development of natural convection in the liquid. A recent study [17] showed the possibility of using Marangoni concentration convection to efficiently mix reagents in a flow reactor. Moreover, the intensity of the convective motion was adjusted to the concentrations of the supplied reagents. The authors have demonstrated that the gravity-dependent convective mechanisms also can be used for effective liquids mixing in microchannels.



In this paper, we show in a series of experiments that double-diffusive instability [18] can be an effective way to mix two solutions in a reaction zone in a form of a long narrow channel. This type of hydrodynamic instability occurs in a two-layer stably stratified system of miscible solutions when the solutes have different diffusivity rates. Several optical methods were used to visualize convective flows and the distribution of mixing substances, which made it possible to estimate the mixing rate along the channel. A significant intensification of mixing is shown in comparison with the purely diffusive case.

2. Experimental set-up

The experimental setup is presented in figure 1. The mixing substances come into the reaction zone through a Y-type mixer forming a two-layer system at the beginning of the zone. The reaction zone has a form of long narrow channel of $d=0.25$ cm height, $h=0.015$ cm width, and $L=7$ cm length. Both inlets are connected by transparent tubes with injection syringes (2). The volume flow rate is carefully controlled through a syringe pump SPLab 02, UNIX Instruments (3). The pump fills the channel with aqueous solutions of two different inorganic salts with equal volume flow rates. Less dense solution of copper sulfate CuSO_4 with mass concentration 6.55 %, density $\rho=1.068$ g/cm³, and dynamic viscosity $\eta=0.013$ g/cm·s were injected through the upper inlet of Y-micromixer and a denser solution of potassium chloride (KCl) with mass concentration 15.45 %, density $\rho=1.1$ g/cm³, and dynamic viscosity $\eta=0.015$ g/cm·s were injected through the bottom one.

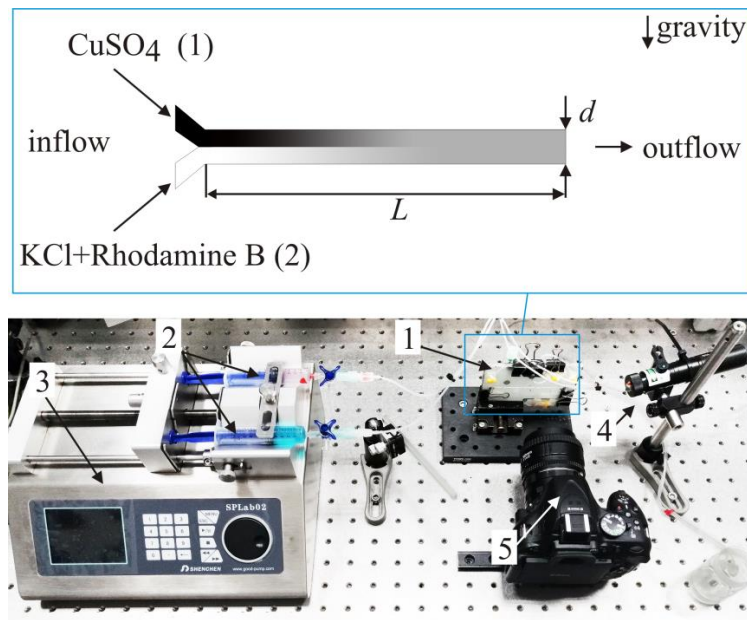


Figure 1. 1 – microchannel with Y-type mixer, 2 – injection syringes connected with inlet tubes, 3 – syringe pump, 4 – laser sheet, 5 – CCD camera.

In order to differentiate the two streams and visualize the mixing process, the fluorescent dye Rhodamine B was dissolved in the KCl solution. The mass concentration of Rhodamine in KCl solution was $5 \cdot 10^{-5}$ %. Such concentration is so low that it does not influence the physical properties of KCl solution. As an illumination source of the channel, we used the laser sheet (4) with wavelength $\lambda=532$ nm. It allows us to see the concentration distribution of the Rhodamine that in the light of the green spectrum fluoresces in the red one. The quantitative analysis of mixing was carried out based on the intensity field of the dye, which is equivalent to its concentration field.

The experiments were carried out for several volume flow rates as shown in table 1. The investigated region of the channel is equal to 3 cm (12d in calibres) and includes initial segment of the mixing channel (the length from the point where two streams combine). During the one test, three consecutive images of the channel with an interval of 1 minute were captured by a high-speed colour camera Nikon 5200 (5). This was repeated for all volume rates. The first image was taken after 30

minutes since the pump started that guaranteed the steady state of fluids flow. To minimize the post-processing error we got the average image that then was converted into grey scale. This procedure is described in detail below. Also in some experiments, the shear interferometry method [19] was used to visualize the structure of convective flows. All experiments were performed at room temperature $(24 \pm 1)^\circ\text{C}$.

Table 1. Parameters of experiments.

Volume flow rate Q (ml/min)	Fluid velocity v (cm/s)	$Re = \rho v h / \eta$
0.002	8.9×10^{-3}	0.010
0.005	22.2×10^{-3}	0.026
0.010	44.5×10^{-3}	0.052
0.015	66.6×10^{-3}	0.079

During the one test, three colour images of the channel were captured at each volume flow rate. All images were then converted into greyscale monochromatic images according to the procedure described in [10, 20]. To get an image with a higher signal-to-noise ratio all images were then averaged to one. Then the background correction was employed. Before each experiment, the image of the empty channel illuminated by the laser sheet was taken. This image served as the background, which was always subtracted (in grey scale) to correct the inhomogeneity of the light sheet intensity. Based on this image, a ready-to-process matrix of gray values was obtained. The Lambert-Beer's law states that the light intensity is linearly depends with the concentration changing i.e. the luminance grey level of the pixel can be converted into normalized depth-averaged dye concentration for this pixel. Thus, the two-dimensional matrix of grey values characterizes the two-dimensional distribution of the Rhodamine concentration. However, to estimate the mixing extent of layers with and without dye, it is not necessary to get the values of the dye concentration. The degree of mixing at a chosen area 1 pixel width and 500 height across the channel length can easily be evaluated by calculation of the mixing parameter M [1, 21]:

$$M = 1 - \left(\frac{\sigma^2}{\sigma_{\max}^2} \right)^{1/2}, \quad (1)$$

where σ is the standard deviation of the grey luminance, and $\sigma_{\max}$ is the maximum standard deviation over the channel. The value of M varies from 0 to 1, with 1 (100 %) indicating complete mixing and values tending to 0 indicating unmixed layers. The standard deviation is calculated using the following equation:

$$\sigma = \left(\frac{1}{N} \sum_{i=1}^N (I_i - \bar{I})^2 \right)^{1/2}, \quad (2)$$

where N is the number of pixels in the chosen area, I_i is the intensity at pixel i , and $\bar{I}$ is the mean intensity of the chosen area. Prior to using the equation (2) the value of σ was always normalized by 0.5.

3. Results

When the solutes in a two-layer system diffuse at different rates the diffusive instability can develop. There are two types of the instability depending on in which layer the solute with a higher diffusion coefficient is dissolved. If the faster component is dissolved in the upper layer, then diffusive-layer convection (DLC) instability arises. In the opposite case, when the lower species diffuse faster, a double-diffusive (DD) instability develops. Here we investigate only the DD instability.

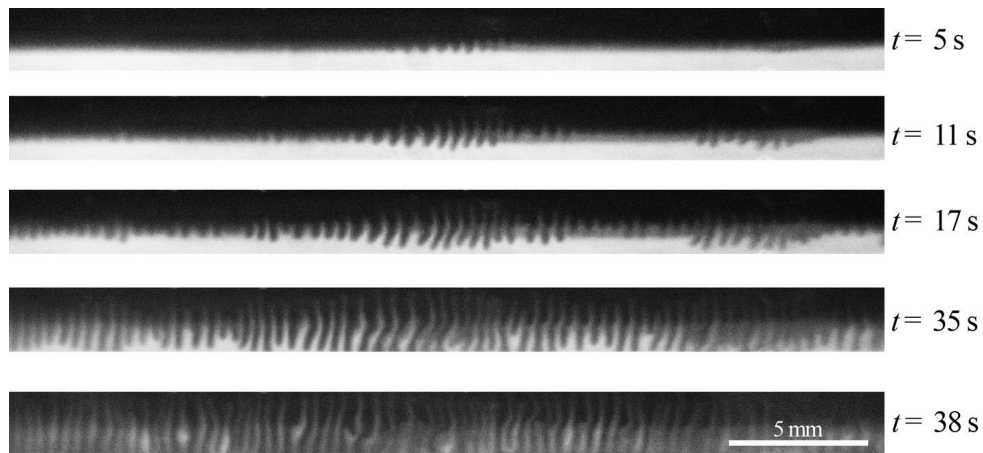


Figure 2. Visualization of the time evolution of concentration field of Rhodamine at $Q = 0$ ml/min. (Raw images that have not yet been processed).

Figure 2 shows the time evolution of the structure of the DD convection without pumping, i.e. at $Q = 0$ ml/min. The images show the distribution of Rhodamine concentration. At the initial moment ($t = 5$ s), the image has a high contrast level. The lower layer has a colour close to white, the upper one – to black. This indicates that Rhodamine is situated only in the lower layer, which means, the initial layers are completely separated. Further, DD convection develops in the form of finger structure symmetrically propagating up and down from the initial contact line. Upward and downward convective currents redistribute Rhodamine in such a way that its concentration in the lower layer decreases and in the upper layer increases.

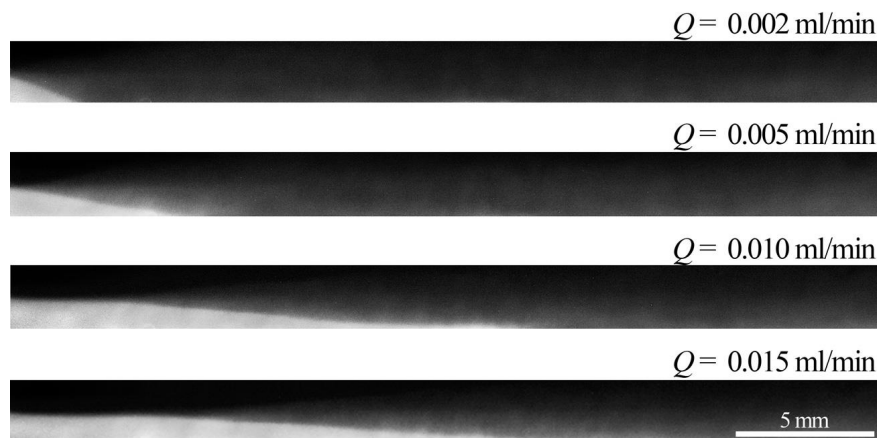


Figure 3. Visualization of the concentration field of Rhodamine for different volume flow rates. (Raw images that have not yet been processed).

The process of the changes of the Rhodamine concentration in both layers is accompanied by a change in the brightness of its luminescence, which makes it possible to analyse the mixing process. Since in this experiment the volume flow rate is zero, the degree of mixing does not change along the channel and depends only on time.

When pumping is turned on the structure of motion is changed. Figure 3 shows the images of the channel obtained for all volume flow rates when the flow was at the steady-state. It is seen that as a flow rate increases, the length of the area, where layers are separated becomes longer. This means that the mixing length also increases with increasing the flow rate. Due to constant pumping, this visualization method does not allow to see the finger structure. For this purpose, we used a shearing interferometry technique.

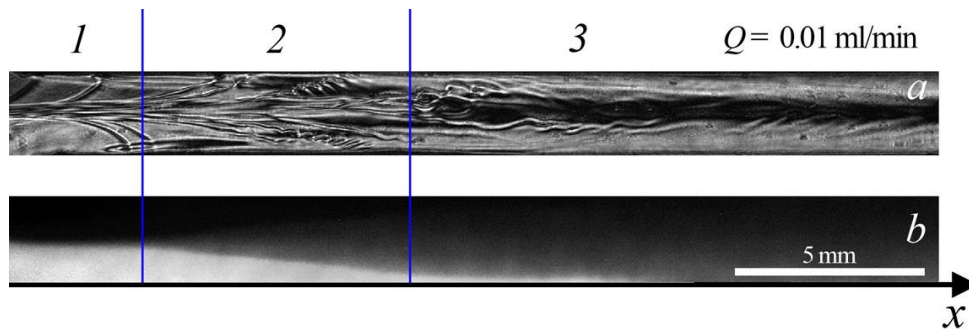


Figure 4. Visualization of the convective structure (a) and the concentration field of Rhodamine (b) at $Q=0.01$ ml/min. (Raw images that have not yet been processed)

Figures 4 (a) and 4 (b) show the images of the channel for $Q=0.01$ ml/min, obtained by the shear interferometer and the dye, respectively. The shear interferometer makes it possible to visualize the distribution of the refractive index derivative. In our experiments the refractive index non-uniformity is caused by variations of solutes concentration, therefore the interferogram patterns reflect mainly a spatial distribution of the derivative of solutes concentration. Since the mass diffusive time is three orders of magnitude larger than the viscous time (Schmidt number $Sc \sim O(10^3)$), the derivative concentration isolines turn out to be trapped by the moving liquid, and the interference fringes move together with the liquid medium. Thus, the study of the interference patterns along the channel allows us to visualize the structure of the convective motion.

The interferogram clearly shows how exactly the finger structure changes when pumping is turned on. Analysis of the shape of the interference fringes allows us to distinguish three characteristic regions along the channel (see 1, 2 and 3 in figure 4). The first area (1) is at the beginning of the channel. Here, two layers of initial liquids are separated by a narrow diffusion zone, which is visualized in the interferogram in the form of many horizontal and not curved fringes. This shape of the fringes indicates the absence of convection, therefore, the diffusion mechanism of mass transfer prevails in this zone. The number of fringes characterizes the magnitude of the density gradient between the layers. Since all fringes are in a very narrow zone it is impossible to count them and quantify the magnitude of the density gradient. The second region (2) is the area of existence of the convective structure. The shape of fringes has become more complex. Near the boundaries of the channel, we observe chaotic vortex structure, which indicate the presence of intense convection. Thus, in this region, convection is the prevailing mechanism of mass transfer; therefore, the process of homogenization of the initial layers occurs from this region. On the image of the dye concentration field (figure 4 (b)) it is clearly seen how strong the difference of the concentration distribution along the vertical axis at the beginning (the layers are separated, each with its own colour) and at the end (the layers are mixed, and an intermediate color between black and white appeared) of this region. Further, in the region (3), the flow structure changes suddenly. On the interferogram we see the one wide horizontal fringe on the background of which a weak convective motion that is visualized as periodic sloping stripes exists. In this region the dominant mechanism of mass transfer is changed from convective to diffusion. At the beginning of this region the homogenization process proceeds very slow, as it is evidenced by minor changes in the interference pattern and weak changes of grey luminance on the image of the dye concentration field. Thus, comparative analysis of the images obtained with the help of Rhodamine and interferometer made it possible to see the flow structure and formally distinguish the areas with convective and diffusive mechanism of mass transfer.

The change of the mixing extent along the channel length was calculated based on the matrix of grey values obtained from image of dye distribution using the equation (2). The mixing parameter M as a function of the distance along the channel measured in the channel height d for different inlet flow rates is shown on figure 5 (a). Dependencies with different colours correspond to results for different flow rates. Experiments have shown that the highest mixing efficiency is achieved at the lowest flow rate $Q=0.002$ ml/min. In this case the convective structure resulting from the formation of the DD convection is located at the very beginning of the channel and takes the zone of several calibres in length.

The vortex motion existing in this region mixes the initially separated fluids rather quickly, which is indicated by a sharp increase in the value of the parameter M . Further, when the convective mixing mechanism changes to the diffusion one, the value of M starts change more slowly. The position of the region where the convective mixing mechanism is prevailing changes due to an increase of the volume flow rate. It also affects the mixing length. Figure 5 (b) shows a dependence characterizing the change in the mixing length required to achieve a mixing of 50 % ($M=0.5$). It is clearly seen that with an increase in the volume flow rate, the value of the mixing length for the same pair of liquids also increases.

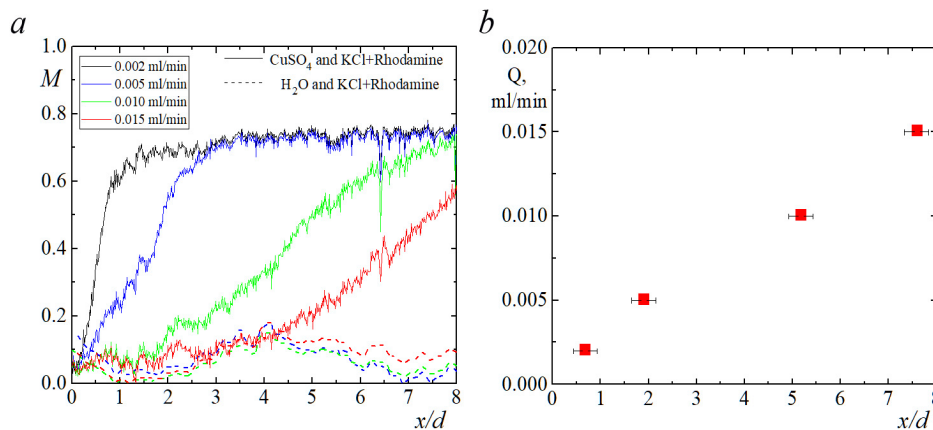


Figure 5. The dependence of (a) the mixing extent on the channel length for different volume flow rates and (b) the mixing length required to achieve 50% mixing, on the volume flow rates.

For comparison, the dashed lines in figure 5 (a) show the results obtained for the two-layer system consisting of aqueous solution of KCl (lower layer) and water (upper layer). In this case, DD instability does not form and a mass transfer provided solely due to diffusion. It is clearly seen that the diffusion mixing mechanism in the geometry under consideration is almost an order of magnitude weaker than the convective one. Also, it worth to note that when the diffusive mechanism is predominant in mixing process the change in the brightness of the dye due to mixing is comparable or even less than the magnitude of the noise, which results in relatively high data spread in the experiments with diffusion mixing.

4. Conclusion

The mechanisms of natural convection that are currently underestimated in microfluidics, can be successfully used for mixing flows in microfluidic devices. We have shown that the DD convection can reduce the mixing length by an order of magnitude in comparison with mixing using a pure diffusion mechanism. The effective mixing becomes possible due to the formation of a complex convective structure that acts like a local mixing tool. The addition of a fluorescent dye made it possible to quantify the mixing degree. It was found that the most mixing efficiency is achieved at the lowest volume flow rate. In this paper, we investigated only one pair of solutions with constant concentrations. However, it is known that by varying the concentration it is possible to change the intensity of double-diffusion convection. In the future, experiments in a more wide range of governing parameters will be performed.

Acknowledgments

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