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Enhancement of mixing inside ionic liquid droplets through various micro-channels design

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ABSTRACT

Ionic liquid (IL, $[C_4mim][BF_4]$) was introduced into micro-channels to form IL droplets and mixing performance inside the droplets was investigated via micro-LIF (laser induced fluorescence) technique. Experiments showed that mixing inside IL droplets generated in a simple cross-junction straight channel was very poor, due to the high viscosity and small diffusion coefficient of IL. To enhance the mixing inside IL droplets, two methods were then proposed. One was to change the way of droplet formation, which was achieved in T-junction and Y-inlet channels. The other was to change the way of droplet movement along the channel, which was achieved in meandering channel and deforming channel. Combing these two methods led to the design of Y-deforming channel, which resulted in excellent mixing inside IL droplets. Because of the extremely slow diffusion rate in IL, the circulation patterns and mixing characteristics within IL droplets were observed clearly in each type of micro-channels. Besides, mixing efficiency was defined and calculated, and its dependence on flow rates and droplet size were discussed in according channels. Based on the qualitative and quantitative analyses, mechanism of the mixing intensification brought by each micro-channel was clarified, and the core was to break the symmetrical circulation pattern inside IL droplets and introduce new vortices to enhance mixing.

1. Introduction

In the continuously growing field of microfluidics, micro-droplet flow, without a doubt, is one of the most attractive and promising subcategories. Apart from the general advantages of microfluidics such as reduced reagent consumption and decreased mass and heat transfer distance, micro-droplet system provides isolated environment with additional internal circulation, which makes those discrete droplets excellent parallel reactors [1,2]. Besides, with the development of auxiliary tools and techniques in mechanical, electrical and other areas, the manipulation of droplets (coalescence, splitting, mixing, sorting, etc.) has become more and more simple and versatile, which greatly expanded the applications of droplet microfluidics. Therefore, literature has reported micro-droplet being applied in high-throughput bio(chemical) analysis[3,4], protein crystallization [5], drug delivery [6], synthesis of functional nanomaterials [7] and so on.

As more and more areas are trying to take the advantages of droplet based microfluidics, the diversity of fluid systems applied in droplet flow also increases, among which ionic liquids (ILs) have attracted our specific attention. Unlike molecular solvents, ILs are composed of ions exclusively. The Coulomb force and hydrogen bond between the anions and cations bring ILs a lot of intriguing features, such as low vapor pressure, high electrical conductivity, special catalytic activity, strong dissolving ability and so on [8]. Therefore, in the short period of time ever since their emerging in mid-1900s, ILs have found a variety of applications in the fields of electricity, catalysis, separation, material synthesis, etc. [9,10]. Multifunctional as they are, ILs also suffer from relatively high viscosity (large transfer resistance) and high cost, which limit their broader industrial applications. To overcome such limitations, some researchers start to put their eyes in microfluidics, especially droplet based microfluidics, since it is advantageous in high mass and heat transfer efficiency and also in reducing reagent consumption. Based on current available literature, the most common ILs involved droplet systems reported for now are water/IL droplet flow systems, where water is the dispersed phase and the hydrophobic IL is the continuous phase [11–15]. Our group also reported that IL ([BMIM] $[BF_4]$) droplets could be generated in PMMA micro-channels with toluene as the continuous phase [16]. Such system is more preferable than water/IL droplet system, because the pressure drop would be much smaller when the highly viscous IL forms droplets instead of continuous phase so that they do not contact with micro-channel walls. On one hand, the advantages of droplet based microfluidics could help to alleviate the drawbacks of ILs. In return, the abovementioned advantages of ILs could also facilitate more complicated droplet formation

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and droplet manipulation in certain ways. Khan et al. created aqueous-IL compound droplets with tunable structures using an imidazolium-based IL and demonstrated their applications for on-drop separation and sensing [17]. Taking advantage of the magnetic response of paramagnetic ILs, Loewe et al. applied those specific ILs in double emulsions and achieved innovative droplet manipulation under magnetic fields in various ways [18].

When dealing with ILs involved systems, the mixing is always critical, which could affect the overall efficiency in many cases [19,20]. As mentioned earlier, mixing in micro-droplet system is superior compared to batch reactor and continuous micro-flow because of the short diffusion distance and internal circulation. However, such internal circulation inside droplets in a straight channel is formed symmetrically along the channel axis, which means there are no perpendicular convection streams to the main flow of the droplet [15,21]. To intensify the mixing inside droplet, Tice et al. used a winding channel to introduce chaotic advection inside droplets to accelerate mixing [22,23]. At each bend of such winding channel, the internal loops were sheared and reoriented (described as “baker transformation”), which broke the symmetry of the circulation loops so that internal fluids mix. Inspired by this idea of flow asymmetry, other microchannel geometries were designed later for optimization of droplet mixing, such as baffled channel (simulation) [21], Z-winding channel (simulation) [24], and bumpy channel (experiment) [25]. In another paper, Tice et al. also pointed out that the initial distribution of unmixed fluid has great influence on the mixing efficiency, and the main point for good mixing is to prevent the initial reagent being distributed in the two parts of symmetrical circulation loops [26,27]. In other words, mixing is more efficient with reagents initially distributed in the front and back halves than that in the upper and bottom halves of droplets [21,28]. Apart from the above method of micro-channel design, active ways have also been explored to enhance the mixing in droplets, such as electrowetting-based droplet mixer [29], light-actuated droplet mixer [30], and droplet mixing in thermocapillary environment [31,32]. Of course additional energy inputs are needed in these active mixing situations.

When ILs become the droplet phase instead of conventional solvent, the mixing performance would be different. The biggest difference comes from the high viscosity of IL, which would affect droplet configuration, diffusion rate and fluid movement inside droplets, all of which could influence mixing inside droplets. Simulation by Stone et al. showed that the mixing efficiency decreases with viscosity ratio (dispersed phase/continuous phase) in a power law relation [33]. In addition, our previous study showed that ILs tend to have strong affinity to channels walls which causes longer tail before droplet break up in T-junction micro-channel [16]. Since mixing is of great importance for ILs involved systems, it is essential to investigate the mixing performance of IL in microfluidic system, especially in droplet based micro-system. Therefore in this paper, we are going to study the mixing behavior inside IL droplets using micro-LIF (laser induce fluorescence) technique. Various micro-channel geometries are designed to enhance the mixing in IL droplets, among which some are innovative, and some are borrowed from literature. But even in the old micro-channels, IL being the droplet phase results in unique mixing phenomena. Mixing patterns of IL droplets in various channels are revealed, and mixing efficiency is quantified and analyzed. Analyses of mixing characterization and influencing factors on mixing efficiency help to disclose the mechanism of mixing intensification in each micro-channel.

2. Experimental

2.1. Materials and microfluidic devices

The droplet system in this work were IL/toluene droplets in PMMA micro-channels, where IL ($[C_4mim][BF_4]$) was the droplet phase, and toluene was the continuous phase. $[C_4mim][BF_4]$ is a typical hydrophilic IL, with viscosity of 66.4 mPa·s (25 °C) and density of 1.21 g/cm^3, and the self-diffusion coefficient of IL is 9.5×10^{-11} m^2/s. Rhodamine B (abbreviated as Rh B in the following) was dissolved in one of the two IL inlets (50 mg/L) as the fluorescence tracer for micro-LIF measurement. IL and Rh B were purchased from Dibo Chemical Technology Co., Ltd. (Shanghai, China).

Six types of micro-channels with different geometries were designed and fabricated to investigate the mixing inside IL droplets (details regarding the structure and operation of each micro-channel will be discussed in the next section). Each micro-channel was fabricated on a 2 mm thick polymethyl methacrylate (PMMA) sample plate by precise milling, and then sealed with another PMMA plate with the same size using a heat press machine (Taikesheng automation system co., LTD, Shenzhen, China). The width of the main channel (w) was 500 μm and the depth (h) was 300 μm unless otherwise stated. Fluids were delivered separately by syringe pumps (Baoding Longer Precision Pump Co., Ltd, Beijing, China).

2.2. Micro-LIF experiments

A microscope equipped with a filter and a 12-bit CCD video camera (IMPERX, IPXVGA210-L, USA) was used for imaging. A 1.5-W diode pumped solid state continuous laser with 532 nm of characteristic wave length (matching the excitation wavelength range of Rh B) was set above the microchannel chip in a fixed angle, which emitted laser and illuminated the micro-channel chip. Then Rh B would be excited and give out fluorescence light. The top view images of fluorescence intensity were recorded at a frequency of 100 fps and spatial resolution of 5 μm/pixel.

The principle of micro-LIF method here is based on the monotonous relationship between the fluorescence intensity and Rh B concentration under laser illumination (verified by experiments). Traditionally, micro-LIF experiments are conducted with only laser source on and microscope light off. This causes difficulty of identifying the droplet boundary in micro-droplet flow when Rh B is not fully distributed in the whole droplet, since there would be no signal where there is no Rh B distribution. The same problem was encountered in our earlier study of mass transfer in water/IL droplet system [14]. At that time we proposed to conduct reference experiments to identify the droplet boundaries. In the reference experiments, the laser source was turned off and the microscope built-in light was turned on and clear droplet boundaries could be observed and recorded. And the determined droplet boundaries were then applied in the corresponding micro-LIF experiments with careful time and position comparison. Although this method was effective, we have to admit that the process is rather tedious and time consuming. In this work, we improved our strategy without the necessity of reference experiments. In current micro-LIF experiments, the microscope light and laser source were turned on at the same time. But the intensity of microscope light was controlled to be rather weak to minimize its effect, meanwhile strong enough to observe the droplet boundaries. Image was recorded as background when there was no Rh B in the system, which would be subtracted from the mixing images as well as calibration images. Because the droplet boundaries were always black (with extremely small gray value) in the micro-LIF images, it was easy to capture the droplet boundaries in this way. With the calibration curve and intensity data from micro-LIF image, the depth-average concentration of Rh B could be obtained. Although details of mixing at different layers of droplet at the vertical direction is missing, we consider that the depth-average concentration data is still capable to provide information on how the distribution of the two initial streams develop inside droplets when they move along the micro-channels. The analyses of images and acquisition of concentration data were all processed using in-house Matlab code.

2.3. Quantification of mixing in IL droplets

Mixing efficiency was evaluated based on the Rh B concentration