Chemical Engineering Science 138 (2015) 128–139

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

Prediction of sizes and frequencies of nanoliter-sized droplets in cylindrical T-junction microfluidics

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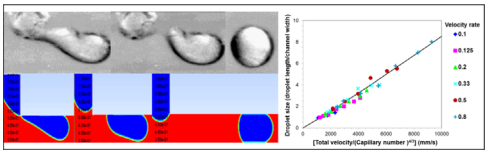
HIGHLIGHTS

- Hydrodynamic of nanodroplets in a microfluidic system using a T-junction.
- Comparison of 3D cylindrical channels with 2D simulations using average velocity.
- Relation between size and frequency of droplets and total velocity, velocity ratio and Ca.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 5 December 2014
Received in revised form
10 July 2015
Accepted 30 July 2015
Available online 10 August 2015

Keywords:
Microfluidic
Drop
Microreactor
Multiphase flow
Hydrodynamics
Fluid mechanics

ABSTRACT

We study the formation of nanoliter-sized droplets in a microfluidic system composed of a T-junction in PEEK and tubing in Teflon. This system, practical for a 'plug and play' set-up, is designed for droplet-based experiments of crystallization with a statistical approach. Hence the aim is to generate hundreds of droplets identical in size and composition and spatially homogeneous. Therefore, parameters of control are droplet size and frequency. However, the geometry of the T-junction is not perfect and, moreover, its channels are circular, as opposed to the planar geometries with rectangular cross-sections that are usually used. However, based on 3D experiments and 2D simulations, we observe the same regimes of droplet generation in circular channels as in planar geometries, and with the same stability. Therefore, we refer to velocities instead of flow rates to characterize the system. Then we define operating range in terms of droplet size and frequency through empirical relations using total velocity, velocity ratio and capillary number, to ensure homogeneous droplets in channels of 500 μm and 1 mm diameters.

1. Introduction

Nanoliter-sized droplets are increasingly used as nano-reactors in chemistry, for crystallization (Li et al., 2006; Selimovic et al., 2009), reaction (Li and Ismagilov, 2010) and analysis (Zare and Kim, 2010; Brouzes et al., 2009; Burns et al., 1998) studies. First, less material is consumed in nanoliter-sized droplets than in milliliter crystallizers. It is important to reduce material consumption when only small quantities of material are available, i.e. rare molecules such as pharmaceutical ingredients, purified proteins, or dangerous materials (energetic materials). Second, generating hundreds of nanoliter-sized droplets permits statistical analysis. Therefore microfluidic technologies are used with two-phase non-miscible flows, through flow-focusing (Gañán-Calvo and Gordillo, 2001; Anna et al., 2003), co-flowing (Umbanhowar et al., 1999; Garstecki et al., 2005) and cross-flowing (Thorsen et al., 2001; Garstecki et al., 2006). In our application, the microfluidic system is dedicated to droplet-based crystallization experiments. Nanoliter volumes makes it possible to nucleate a limited number of crystals that we can locate easily, and the generation of hundreds of nanoliter-sized droplets allows stochasticity of nucleation to be addressed Candoni et al. (2012). Therefore, our purpose is to generate hundreds of droplets identical in size and composition. Moreover, as we mix different solutions before the generation of

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http://dx.doi.org/10.1016/j.ces.2015.07.046
0009-2509/

droplets, the droplets' spatial homogeneity is also a crucial consideration.

In this paper, we study a 'plug and play' microfluidic system composed of a T-junction in PEEK and tubing in Teflon. Droplets are generated by cross-flowing the crystallization solution and the non-miscible oil, which is the continuous phase. The advantage of both Teflon and PEEK polymers over PDMS, which is only compatible with water, is their compatibility with organic solvents such as ethanol, acetone or nitrobenzene (Ildefonso et al., 2012). We choose ethanol as crystallization medium in order to ensure maximum versatility; we use as continuous phase fluorinated oil FC-70 which has no or very low miscibility with solvents like ethanol and good wettability with Teflon. Hence the shear of the continuous phase, which is injected into the junction perpendicular to the dispersed phase, leads to the break-up of dispersed phase droplets. We use Nemesys pumps to inject the continuous and the dispersed phase with reproducible flow rates, allowing us to generate droplets of the dispersed phase identical in size and frequency. Mixing inside droplets after their break-up is accelerated by the flow of the continuous phase if droplets can twirl in the channel, and hence the droplets are spatially homogeneous. But this twirling requires spherical droplets, which means that droplet diameter must be smaller than or equal to the channel diameter. However, droplets smaller than channel diameter can move in the channel and coalesce, depending on the frequency at which they are generated. The minimum droplet size must therefore be of the order of channel diameter and the frequency must be low.

The literature contains many experimental studies and simulations investigating the size of droplets. To the best of our knowledge, the studies presented in the literature use planar geometries with rectangular cross-section typically between 50 and 300 μm. They explore phase properties (viscosity (Garstecki et al., 2006; Xu et al., 2008; Christopher et al., 2008; Liu and Zhang, 2009; Gupta and Kumar, 2010; Glawdel et al., 2012a, 2012b; Chen et al., 2011; Wehking et al., 2013) and surface tension (Thorsen et al., 2001; Xu et al., 2008; Wehking et al., 2013), channel geometry (the height and the width of the channels (Garstecki et al., 2006; Glawdel et al., 2012a, 2012b; Wehking et al., 2013; Van Steijn et al., 2010)) and operating parameters (flow rate ratio (Garstecki et al., 2005, 2006; Xu et al., 2008; Christopher et al., 2008; Liu and Zhang, 2009; Gupta and Kumar, 2010; Glawdel et al., 2012a, 2012b; Chen et al., 2011; Van Steijn et al., 2010; Tice et al., 2003; Zhao and Middelberg, 2011)). Droplet size is shown to be influenced by flow rate ratio and capillary number (Garstecki et al., 2006; Xu et al., 2008; Christopher et al., 2008; Liu and Zhang, 2009; Wehking et al., 2013; Van Steijn et al., 2010; Tice et al., 2003; Zhao and Middelberg, 2011) (Ca). Moreover flow velocities are generally used instead of flow rates to represent droplet parameters (Xu et al., 2008; Christopher et al., 2008; Glawdel et al., 2012a, 2012b; Chen et al., 2011; Tice et al., 2003; Nisisako et al., 2002). To date, four distinct regimes of droplet formation or break-up within the confined geometry of a microfluidic T-junction have been described in the literature: squeezing, transient, dripping and jetting (Thorsen et al., 2001; Garstecki et al., 2006; Xu et al., 2008; De Menech et al., 2008). At low Ca, squeezing operates as a rate-of-flow-controlled regime, break-up arising from the pressure drop across the emerging droplet in the channel (Garstecki et al., 2006). At $Ca > 0.01$, dripping operates, shear stress playing an important role in break-up (Thorsen et al., 2001). Jetting operates at very high flow rates and/or with low surface tension (De Menech et al., 2008). An intermediate regime between squeezing and dripping, named transient, is observed by Xu et al. (2008) for $0.002 < Ca < 0.01$, in which break-up is controlled by both pressure drop and shear stress. But most authors did not use a transient regime and worked with a critical Ca of ≈ 0.015 to define the transition between squeezing and dripping (De Menech et al., 2008). In contrast, few studies deal with droplet frequency (Christopher et al., 2008; Gupta and Kumar, 2010; Wehking et al., 2013) even though it is easy to calculate using experimental results from the literature.

Our microfluidic configuration is easy to build and to use (Candoni et al., 2012; Ildefonso et al., 2012); it has circular channels, and the T-junction is not intended to be used for microfluidic experiments because its geometry is not perfect. Thus in this paper, we compare our non-perfect T-junction with circular channels to purpose-designed planar geometries with rectangular cross-sections molded in PDMS. We investigate the effect of total flow rate, flow rate ratios and capillary numbers on both droplet size and frequency. The aim is to define the operating range through empirical relations to ensure homogeneous droplets in channels of 500 μm and 1 mm diameters.

2. Material and methods

2.1. Experimental set-up

The microfluidic system (Fig. 1a) is composed of two tubings of identical internal diameter W (W is either 500 μm or 1 mm) made of Teflon. They are connected in a T-junction from IDEX in PEEK (polyether ether ketone) at right angles. The main channel contains the continuous phase (oil) whereas the orthogonal channel contains the dispersed phase (ethanol). The inner diameter of the T-junction is identical to that of the tubings, i.e. 500 μm or 1 mm (Fig. 1b).

The continuous phase and the dispersed phase are separately loaded using separate syringes placed in a syringe pump (neMESYS), which generates extremely smooth and pulsation-free fluid streams from 0.01 μL/s. The two phases are injected with given flow rates as follows: 0.15–12.3 μL/s for the continuous phase (Q_C) and 0.03–6.2 μL/s for the dispersed phase (Q_D). The ratio between the dispersed and the continuous flow rates (Q_D/Q_C) is varied from 0.1 to 0.8 and the total flow rate Q_{TOT} ($=Q_D+Q_C$) is varied from 0.28–14 μL/s. Variation in droplet size is 5% of the mean diameter, corresponding to 15% in terms of volume. However this variability is

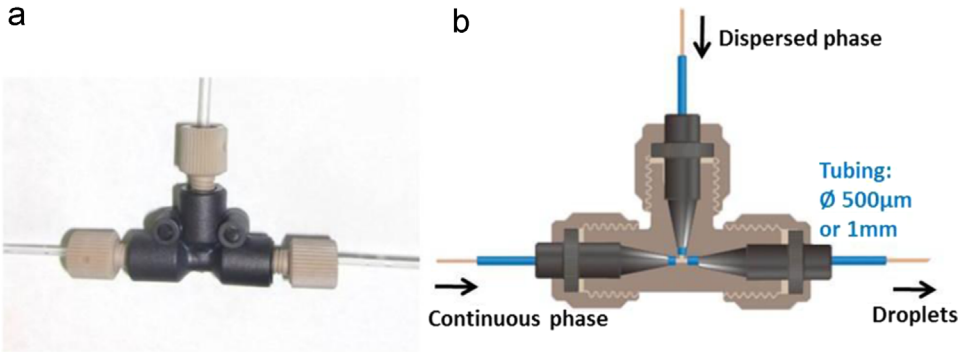

Fig. 1. (a) Photo and (b) scheme of PEEK T- junction from IDEX Health and Science catalog.