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Interfacial precipitation and clogging in straight capillaries

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HIGHLIGHTS

- Clogging of straight capillaries during interfacial precipitation was studied.
- The interfacial precipitation system comprised of saturated salt solution and acetone.
- A wide range of flow regimes were observed and corresponding clogging time was monitored.
- Individual slugs were tracked in real time and the dynamics of precipitation were monitored.
- In slug flow regime, solid shells were observed at the rear end of acetone slugs.

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ABSTRACT

Clogging of straight capillaries during interfacial precipitation (of common salt from saturated salt solution and acetone) was studied for a range of conditions that result in different flow regimes. The particle formation and clogging was explored using the images obtained by tracking a moving slug in real time. The flow regimes varied along the capillary length due to continuous mass transfer of acetone to water resulting in elongation of continuous phase slugs. In the slug flow regime, the precipitated particles formed solid shells/hemi spherical caps at the rear of acetone slugs, which eventually get detached from the interface. In the wavy parallel flow regime, where the interface is not flat, salting out was almost instantaneous and it led to faster clogging of the channels. Smaller *Ca*, i.e. lower flow rates or the use of smaller capillary length or using continuous fluid of relatively higher viscosity or lower interfacial tension can help to avoid or delay clogging. Formation of cohesive shells at the rear of a slug delayed clogging in the capillaries by delaying settling of individual particles. Parallel flow regime with a flat interface delayed the clogging significantly due to poor mass transfer as well as higher superficial velocities.

1. Introduction

In the recent time, microreactors and miniaturized devices have markedly changed the synthesis approach for high value low volume chemicals involving exothermic as well as multiphase reactions limited by interfacial mass transfer (Abolhasani et al., 2015). Small channel size (hydraulic diameter d_h) offers very high mixing, mass transfer and heat transfer area per unit volume ($a=4/d_h$), which further helps in efficient heat transfer. Although these features are exciting and every year the number of new examples of flow syntheses is increasing exponentially, the approach poses severe challenges for the reactions where the product or byproduct or an intermediate is a solid. Primary reasons for avoiding the systems involving flow of suspension in small channels are: Small channel sizes, large area per unit volume available for deposition of solids and the laminar flow of liquid that may not impose sufficient convective force on (lighter or heavier) particles. Such a situation usually results in partial or complete clogging of channels by the particles generated during reactions or due to varying solubility of the reaction mixture from inlet of the reactor to its outlet. A few such examples include: Pd-catalyzed amination, Grignard reactions, aromatic nitrations, catalytic hydrogenation, Nef oxidation, polymerization reactions etc. (Hartman, 2012). Many of these reactions involve more than one phase and in several cases the reactions are instantaneous and they generate solids at the interface. The clogging process is extremely complicated and probably random due to various complex

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Notations

θ_{clog}	Clogging time(s)
Q_T	Total flow rate (ml/min)
Re	Reynolds Number (dimensionless)
Bo	Bond Number (dimensionless)
g	Gravitational acceleration (cm/s^2)
L	Characteristic length (cm)
d	Capillary Diameter (cm)
$\Delta\rho$	Density difference between wetting and non-wetting phases (gm/cc)
σ	Surface Tension (Dyne/cm)
γ	Shear rate (s^{-1})
c	Molar concentration(moles/cm^3)
D	Diffusivity (cm^2/s)
u	Superficial velocity (cm/s)
k_La	Overall mass transfer coefficient (s^{-1})
Ca	Continuous phase capillary number (dimensionless)

inter-dependent phenomena involved in it and it is dynamic in nature. A few excellent reports on clogging of small channels acknowledge the complexity involved in this phenomena (Hartman et al., 2010; Sharp and Adrian, 2005; Wyss et al., 2006). In addition to clogging, generation of solids also adds a new phase to the reaction mixture resulting in change of flow regimes spatially.

Due to the complexity involving relative rates of various parallel and sequential phenomena and stochastic nature of the clogging process no unified mechanism can predict the clogging time. Wyss et al. (2006) have reported that the average number of particles that can pass through a pore before it clogs plays a decisive role independent of both flow rate and particle volume fraction. It is a well accepted norm that the mechanism of clogging involves the random occurrence of local particle aggregation leading to large agglomerates, which are large enough to result in physical blocking of channels (Goldsztein and Santamarina, 2004). Arch formation within a capillary/microchannel, where the particles also have a noticeable adhesive effect on the channel wall (Sharp and Adrian, 2005) is also observed. For very large *Pe*, shear plays a role in bringing particles close to each rather faster than Brownian motion, which enhances the aggregation rate and hence results in clogging of microfluidic devices. Formation of agglomerates or clusters close to the channel wall plays an important role on initializing clogging (Gudipaty et al., 2010). While the literature helps to know the possible mechanisms for clogging in a channel, it does not help in developing a quantitative analysis of when to expect clogging in small channels and the associated time scales for different flow regimes. In order to explore these features in a quantitative framework, the present work aims at exploring the clogging time for different flow regimes for a specific case of interfacial precipitation.

One of the ways to generate the solid particles in a controlled manner in a microchannel is by precipitation using an antisolvent (Ali et al., 2009; Su et al., 2007; Zhao et al., 2007; Zhu et al., 2010). When organic and aqueous phases enter into a microchannel, the large interfacial area as well as very small diffusion path length help to enhance the interfacial mass transfer (Hisamoto et al., 2001; Wang et al., 2002; Zhao and Middelberg, 2011). Use of an organic phase having high solubility in the aqueous phase helps rapid precipitation of the solute (typically a water soluble salt) dissolved in the aqueous phase. This approach has been reported for the synthesis of proteins (Zhang et al., 2015), magnetic materials (Lee et al., 2012), hollow capsules of inorganic (Liu et al., 2009), metal-organic materials (Ameloot et al., 2011), bio nanoparticles (Russell et al., 2005) and nano-precipitation of steroids like methyl prednisolone (Ali et al., 2009). Although these examples provide important insights into interfacial precipitation and an equally important application of microfluidic devices for on demand synthesis, the effect of the flow regimes on possibility of their agglomeration and subsequent blockage dynamics in a capillary/microchannel are not investigated.

This work provides an insight into the microchannel clogging mechanism in liquid–liquid multiphase flow. Here we explore the effect of flow rates of the fluids and capillary diameters on clogging time during interfacial precipitation. We also aim to determine the influence of (i) various flow regimes and (ii) the associated dynamics viz. coalescence of dispersed phase during the flow and the nature of interface on clogging time. In view of this, the present manuscript is organized as follows: after Introduction, we have given the details of experiments and the experimental set-up. Subsequently, effects of various parameters viz. flow regimes, interfacial area, coalescence, capillary number on clogging time is presented. A model is presented that helps to estimate the extent of mass transfer of anti-solvent into the solvent and predicts the solute equilibration time t_0, which can be correlated with the experimentally measured clogging time. The predictions of equilibrium time obtained from simulations were compared with the clogging time. Finally, we conclude by giving quantitative information that will help to select the right set of conditions that can help avoid clogging in such systems.

2. Experimental setup and procedure

The experiments aim at measurement of clogging time in straight glass capillaries. Saturated salt (NaCl) solution of water and acetone were pumped in the capillary. Acetone acts as an antisolvent and it resulted in salting out of NaCl particles along the capillary length. The process of precipitation goes through nucleation and growth stages. Beyond a certain particle size, depending upon the flow rates, once the gravitational force/settling velocity becomes higher than the convective flow, the particles can settle in the capillary. Straight glass capillaries with a specific inlet arrangement (Fig. 1) were used for these experiments. Among the three inlets, two were connected to syringe pumps (Holmarc Optomechatronics, India) and the third inlet was connected to a digital manometer (AZ Instruments, China) to monitor the transient pressure buildup as the capillary undergoes clogging. The saturated salt solution and the antisolvent were introduced at equal flow rates (0.2 –5 ml/min) through the first and the second inlet, which forms the continuous and dispersed phase, respectively. Fig. 1 shows the arrangement of inlet section for both the phases, where the dispersed phase slugs/drops are sheared off by the cross-flowing continuous phase (Fig. 1). With the above range of flow rates it was possible to change the residence time in the capillary by 25 times. Capillaries of four different diameters ranging from 0.88 to 3.62 mm were used for these experiments and were positioned in a perfectly horizontal manner. A digital microscope with high-speed camera (Zeiss Stereo Discovery v2.0) was used to get high-resolution images of precipitating interface and the nature of salt agglomeration. A high-resolution camera (Sony SLT-A37K) was used for monitoring the liquid–liquid flow regimes (at a distance of 15 cm from the inlet) and the time scales of precipitation resulting in clogging inside the capillaries. In order to monitor the interfacial precipitation happening over a specific slug as it moves in the capillary a double rail traversing system was