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Investigation of a microfluidic approach to study very high nucleation rates involved in precipitation processes

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HIGHLIGHTS

- Fast nucleation rates were measured in a droplet-based microfluidic system.
- The nucleation rate of neodymium oxalate is found to increase with time.
- The chip design enables to decouple nucleation from mixing.
- Huge supersaturation ratio can be reached without nucleation.

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ABSTRACT

A microfluidic device has been specially developed to enable the study of fast nucleation kinetics involved in precipitation processes. This setup allows drops of two different reagents to be generated synchronously and to coalesce, and ensure the mixing of their reactants within few milliseconds. The results presented in this paper show that droplet based microfluidic devices are promising tools for studying high nucleation rates involved in precipitation processes. By using the stochastic nature of the nucleation process and the effect of the confinement on the induction time, a tailored microfluidic device has been used to measure nucleation rates as high as $J=7.68\times10^{13}\ m^{-3}\ s^{-1}$. Moreover, kinetic data deriving from nucleation experiments were found in good agreement with data deriving from "conventional" technics.

1. Introduction

As introduced by Söhnel and Garside (1992), precipitation is a fast crystallization process, taking place at very high supersaturation. As a result, very high number (from 10^{10} to 10^{16}) of small crystals (from 10 nm to 10 μm) are produced. Moreover, as precipitation usually results from a fast chemical reaction, the role of mixing is of paramount importance (Söhnel and Garside, 1992; Baldyga and Orciuch, 2001). Because precipitation processes are prevalent in many chemical industries, a large amount of studies in the literature deal with the determination of the nucleation kinetics, growth rates, aggregation and agglomeration rates involved in these processes (Roelands et al., 2006). It appears from the literature review that the main and more relevant experimental technique to measure nucleation rates, relies on rapid mixers (vortex mixers like Hartridge–Roughton mixers, or *T* mixers) that achieve mixing time as low as a few hundred of microseconds. This low mixing time is assumed to be lower than the induction time required for nucleus formation in the supersaturated solution (which is typically around 1 ms or lower), and nucleation rates are derived from the number of particles produced. The latter can be determined either by optical techniques (*i.e.* a laser measuring the scattered light at the outlet of the mixer) or by quenching the suspension in a gel, in order to prevent further nucleation or crystal growth before counting the crystals (Bertrand-Andrieu et al., 2004; Lindenberg and Mazzotti, 2010). Both approaches are effective, and have generated most of the results available in the literature, but they are product consuming, and thus inappropriate for high added value products or for dangerous species like in the nuclear industry. In addition, because the crystals are analyzed a long time after their generation, relevant information regarding the nucleation process can hardly be derived from the final properties of these crystals.

In the last decade, microfluidic systems have proven to be reliable experimental tools for studying nucleation kinetics of proteins (Shim et al., 2007; Akella et al., 2014), salts (Laval et al., 2007), organic molecules (Dombrowski et al., 2007; Teychene and

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Biscans, 2012). In these studies, the authors have used microfluidic systems to generate monodispersed droplets, each of them containing both the solvent and the solute to crystallize, and both flowing in an inert fluid. Supersaturation inside the droplets was generated by cooling down the system below the solubility temperature. The number of empty droplets and of droplets in which one or several crystals are present is then monitored over time. Assuming nucleation is a stochastic process, it can be described by a Poisson distribution (Pound and La Mer, 1952; Goh et al., 2010), from which kinetic can be derived. These works revealed that microfluidic is a powerful technique for studying nucleation. However, only "slow nucleation processes", in which mixing is not critical and occurring at low supersaturation ratio ($S=C/C_{sat}<20$), have been examined.

The present work focuses on the relevance of microfluidic tools for studying the high nucleation rates encountered in reactive precipitation. A specific microfluidic configuration was designed and used to measure nucleation kinetics in the case of oxalates precipitation, as implemented in hydrometallurgical processes, and as recently studied by Charton et al. (2013). The main idea of this study is to take advantage of the increase of the induction time with the decrease of the solution volume V. Indeed, according to the classical nucleation theory, the induction time (*i.e.* the time needed for the first crystal to appear in a supersaturated solution), scales with V^{-1}, meaning that if the solution volume is low enough, the time-scales for the nucleation and mixing processes can be separated. For instance, based on the nucleation kinetics of neodymium oxalate measured with the classical "rapid-mixer" methodology (Bertrand-Andrieu et al., 2004) assuming a typical supersaturation ratio of $S=29$, and according to Chen et al. (2012), a simple calculation yields mean induction times of 1 μs and of 250 ms for solution volume V of 1 ml and 1 nl, respectively. Consequently, a microfluidic chip has been designed to (i) generate droplets with volume ranging from 0.5 nl to 1 nl, (ii) achieve quick mixing of the reactants inside the droplets after their fusion ($t_{mix}\sim 10$ ms), and (iii) ensure proper flow of the droplets in all parts of the system and at all time (*i.e.* to avoid channel clogging). To attest the relevance of this setup for the experimental investigation of fast nucleation events at high supersaturation ratio, two important issues must be addressed: Can nucleation be efficiently decoupled from mixing? Is it still possible to observe and to measure the stochastic nature of the nucleation process?

2. Material and methods

2.1. Fluids and reagents

Regarding the precipitation experiments, the following fluids and reagents were purchased from Sigma Aldrich: Neodymium nitrate hexahydrate ($2Nd(NO_3)_3$, $6H_2O$, purity: 99.9%), oxalic acid dihydrate ($H_2C_2O_4$, $2H_2O$, purity > 99.5%), nitric acid (HNO_3, 70%), 1*H*–1*H*–2*H*–2*H* perfluorodecyltrichlosilane (FDTS, purity: 97%), 1*H*,1*H*,2*H*,2*H*-perfluoro-1-octanol (PFO, purity: 97%), 2,2,4-trimethylpentane (purity > 99.5%).

Regarding specific materials required for the chips' production: Norland Optical Adhesive N°81 (NOA-81) was purchased from Edmund Optics; Polydimethyl siloxane (PDMS) was purchased from Ellsworth Adhesive Europe and SU8 2150 was purchased from Microchem.

All the reagents were used without further purification.

2.2. Interfacial and surface tension measurements

Interfacial tension was measured with a commercial drop shape analysis system (DSA100S, Krüss), equipped with camera. DSA software fits the digital drop profile to a numerical solution of the Young–Laplace equation. 50 μl Hamilton syringes (Harvard Apparatus) pre-filled with the fluorinated oil and perfluorooctanol were used to produce 2 μl hanging drops on the beveled tip of a 22 ga needle (Hamilton) immersed in a glass cell (Hellma), filled with aqueous solution. The measurements were performed at 23 °C.

Contact angle measurements were performed using the same apparatus operated in the sessile drop mode. A droplet of 50 μl was deposited on the surface, and the shape of the droplet was measured using the built-in image treatment software (DSA software). The experiments were performed at 23 °C.

2.3. Design of the microfluidic chips

Fig. 1 presents a schematic of the microfluidic chip that has been built. It is divided into four sections, each one dedicated to a given function.

The first portion is dedicated to the generation and synchronization of a pair of drops, one drop of each reagent. Droplets of each reactant are generated by two T-junction ① allowing a reproducibility of 97% regarding the volume of each droplet (Gu et al., 2011). The pair of droplets is synchronized thanks to a pressure oscillator ② and an oil by-pass ③ (Hong et al., 2010). Indeed, the pressure oscillator allows droplets to be generated alternatively on the one and the other T-junction, while the oil bypass ensures synchronization of the droplets pair by balancing the flow velocity between each channel. The second part consists in a Y-junction ④ wherein droplets coalescence occurs. The details of the hydrodynamic design of the microfluidic chip is similar to the ones found in Hong et al. (2010).

To study nucleation and to decrease the mixing time of the content of the merged drop (Sarrazin et al., 2007), a winding channel ⑤ has been added to the design developed by Hong et al. (2010).

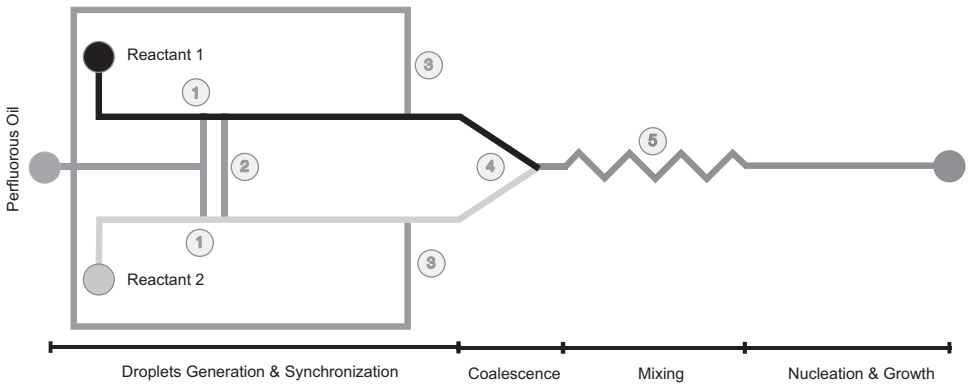

Fig. 1. Schematic of the microfluidic chip design. ① T-junctions; ② pressure oscillator; ③ oil by-pass; ④ Y-junction (droplets fusion); ⑤ winding channels (mixing).