EFFECT OF SURFACTANTS ON CALCIUM CARBONATE CRYSTALLIZATION IN MICROCHIPS UNDER VARIOUS WETTABILITY CONDITIONS

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ABSTRACT

Calcium carbonate formation during supersaturated solutions flow ($NaHCO_3$ and $CaCl_2$) in microchips, at low Reynolds values (Stokes flow), was found to be affected by wall surface wettability, the presence of organic phases miscible or immiscible with the aqueous phase, fluid flow velocity, supersaturation ratio values etc. The time of observation of the first crystal, the crystal growth rate as well as the prevailing polymorph varied depending on the surface wettability and the presence of organic phases. N-dodecane forming oil-water interfaces accelerated crystal formation, showing that oil-water interfaces played the role of nucleation sites. Surfactants are usually used to enhance the displacement of organic phases immiscible with aqueous phases by decreasing water-oil interfacial tension or by altering the oil-wet rock behavior. Moreover, surfactants were found to inhibit crystal formation. In this work, two different surfactants, an anionic (Aerosol OT, i.e. Dioctyl sulfosuccinate sodium salt) and a neutral surfactant (CTAB, i.e. Cetyltrimethylammonium bromide) were dissolved in the supersaturated solutions at various concentrations. Their effect on crystal formation and growth was investigated during the flow of the solutions for various supersaturation ratio values in glass and silane coated glass microchips. The rate of crystal growth, the time of the first observed crystal and the morphology of formed crystals gave information on prevailing crystal formation mechanisms.

KEYWORDS: Surfactants, calcium carbonate, microfluidic, wettability, crystal

INTRODUCTION

Surface wettability is a property strongly dependent on the physicochemical affinity of the respective material with a fluid or a system of fluids [1]. In oil and gas industry, pore surface wettability plays a significant role in oil or gas entrapment in pores of reservoirs [2-3]. The hydrophobic nature of the pore surface in carbonate rocks results in low oil recovery efficiencies, and significant amounts of oil trapped during waterflooding. Several techniques, such as use of smart water, nanoparticles, or surfactants, etc., are used to modify interfacial tension of fluid system and enhance these processes [4]. Previous studies in microchannels showed that during calcium carbonate precipitation, wettability affects crystal nucleation and growth[5]. Moreover, the presence of organic phase immiscible with water, and thus the existence of oil-water interfaces resulted to the stabilization of calcium carbonate polymorphs: vaterite, aragonite and the thermodynamically most stable calcite and accelerated crystal nucleation and growth[6]. Surfactants are amphiphilic molecules which are consisted of an hydrophilic and an hydrophobic part. The hydrophobic part is consisted of one or more aliphatic chains while the hydrophilic part is consisted of ionic and nonionic polar parts. Surfactants were found to inhibit crystal formation[7]. Mechanisms of surfactant EOR mainly include decrease of interfacial tension (IFT) and improve of reservoir wettability toward strong hydrophilicity. Entrapped oil is immobile due to the surface tension between oil and water and when the operating pressure cannot overcome the critical capillary pressure to displace entrapped oil, surfactants are used to reduce the interfacial tension, thereby

the critical capillary pressure decreases, and water displaces trapped oil. Furthermore, surfactant may increase hydrophilicity of the reservoir pore surfaces displacing oil films attached on the pore walls, thus decreasing residual oil saturation and enhancing oil recovery [8]. In this work, calcium carbonate precipitation was investigated by mixing supersaturated solutions under flow conditions in hydrophobic and hydrophilic microchips in the presence of two different surfactants; AOT (40 ppm) and CTAB (20 ppm) in the absence of organic phases. The precipitation of $CaCO_3$ in glass and silane coated microchips was investigated for supersaturation ratio values equal to SR=30.2 and 50.7. The precipitated calcium carbonate crystallites were monitored using a camera (Axis 223 M network camera). The time of observation of the first crystal and the crystal sizes as function of time were recorded.

METHDOLOGY

Calcium carbonate precipitation from the flow of supersaturated solutions in the presence of surfactants was investigated in glass and silane coated microchips of Y-junction topology with two inlets and two outlets (Dolomite, Royston, UK) (Figure 1) at room temperature (~25 °C) at a constant mean total flow rate 0.5μL/min (flow velocity 2.53×10^{-4} m/s, Re=0.052, laminar Stokes flow). The characteristics of the microchip are summarized in Table 1. The hydrophilic microchips were made of B 270® type glass and the hydrophobic microchips consisted of a monolayer of silane groups on the B 270® type glass. Sodium bicarbonate solution was prepared by dilution of stock solution. In the case of calcium chloride with addition of CTAB, first calcium chloride solution was prepared by dilution of stock solution and then the appropriate amount of CTAB was added while stirring the calcium chloride solution at low rates. For the preparation of calcium chloride solution with AOT the appropriate quantity of AOT powder was dissolved in 80 mL of sodium chloride in a volumetric flask 100 mL and the solution was heated in the oven at 40 °C overnight. Next, the solution was left to environmental temperature for 2 hours and the appropriate amount of calcium chloride was added. Finally, 20 mL of sodium chloride were added. The ionic strength of the solutions was adjusted to 0.15M using the appropriate amounts of sodium chloride stock solution, prepared from the respective crystalline solid.
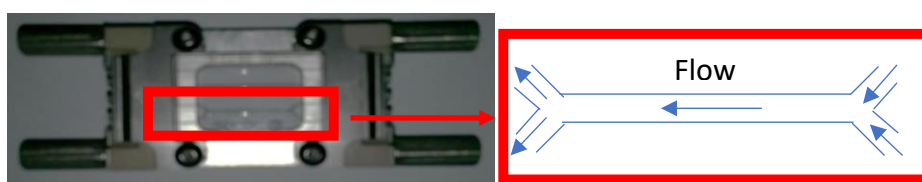

Figure 1. *Microchip used in the precipitation experiments.*

Table 1. *Characteristics of microchips*

Characteristics of microchips	
Width (μm)	205
Length between Y Junction (cm)	1.5
Height (μm)	100
Volume between Y Junction (μL)	0.2
Microchip's volume (μL)	0.36

Surface roughness (nm)	5

Microchips were cleaned following a sequence of injections: HCl solution, deionized water, acetone, deionized water, ethanol, and air according to manufacturer's instructions. For the glass microchip, solution HCl (1 M) was used. The silane coated microchips were washed using HCl solutions (0.08 M) to avoid wettability changes of the microchips according to the instructions of the manufacturer (Dolomite, Royston, UK). The cleaning procedure was repeated until no crystal was observed, and the effluent's pH value was ~7.0. The used experimental set-up is described in detail elsewhere. [5,9] The experiments were conducted in SR values 30.2 and 50.7.

RESULTS & DISCUSSION

In the case of glass microchips in the presence of AOT = 40 ppm for SR values equal to 30.2 and 50.7 the first crystals were observed after 1.5 and 0.5 hours from the start of the experiment (Figure 2). In the absence of AOT[5], the time of observation of the first crystals were 24 hours for SR = 30.2 and 8 hours for SR = 50.7. In the presence of AOT = 20 ppm[9] the time of observation of the first crystals were 1 h for both SR values. Apparently, the presence of AOT accelerated crystal formation in the glass microchips. In the absence of AOT the only polymorph of precipitated calcium carbonate was calcite. The presence of AOT in both SR values resulted in the formation of less stable polymorph such as vaterite and in the higher SR value vaterite dominated.
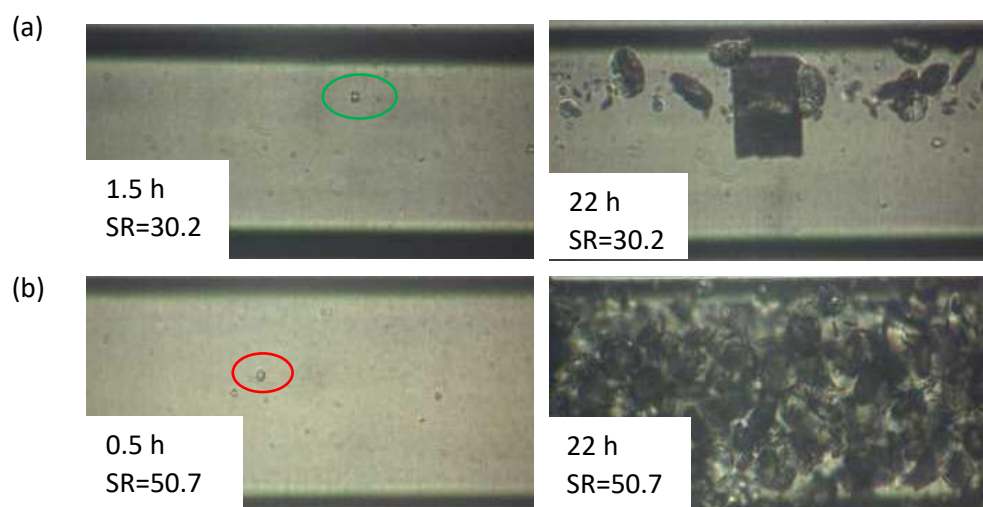

Figure 2: *Snapshots from the first observed crystals during CaCO₃ precipitation in hydrophilic microchips in the presence of AOT 40 ppm: (a) SR = 30.2 , (b) SR = 50.7.*

In the case of the silane coated glass microchip, at SR = 30.2, the presence of AOT = 40 ppm resulted in inhibition of calcium carbonate nucleation compared to the corresponding experiment in the absence of AOT and in the experiment with AOT = 20 ppm (Figure 3a). 24 hours past the initiation of the experiment, inhibition of crystal growth and secondary nucleation was observed along the entire length of the hydrophobic microchip that resulted in the formation of a smaller number of larger size crystals (Figure 4). At higher SR value (50.7) in the presence of AOT = 40 ppm , the time of the first observed crystal did not change significantly but the secondary nucleation and crystal growth were favored (Figure 3b).
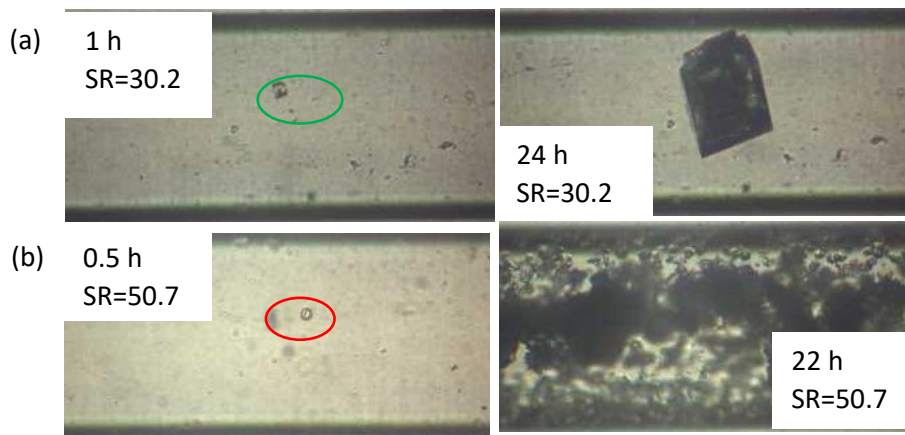
Figure 3: *Snapshots from the first observed crystals during CaCO₃ precipitation in silane coated microchips in the presence of AOT 40 ppm: (a) SR = 30.2 , (b) SR = 50.7.*
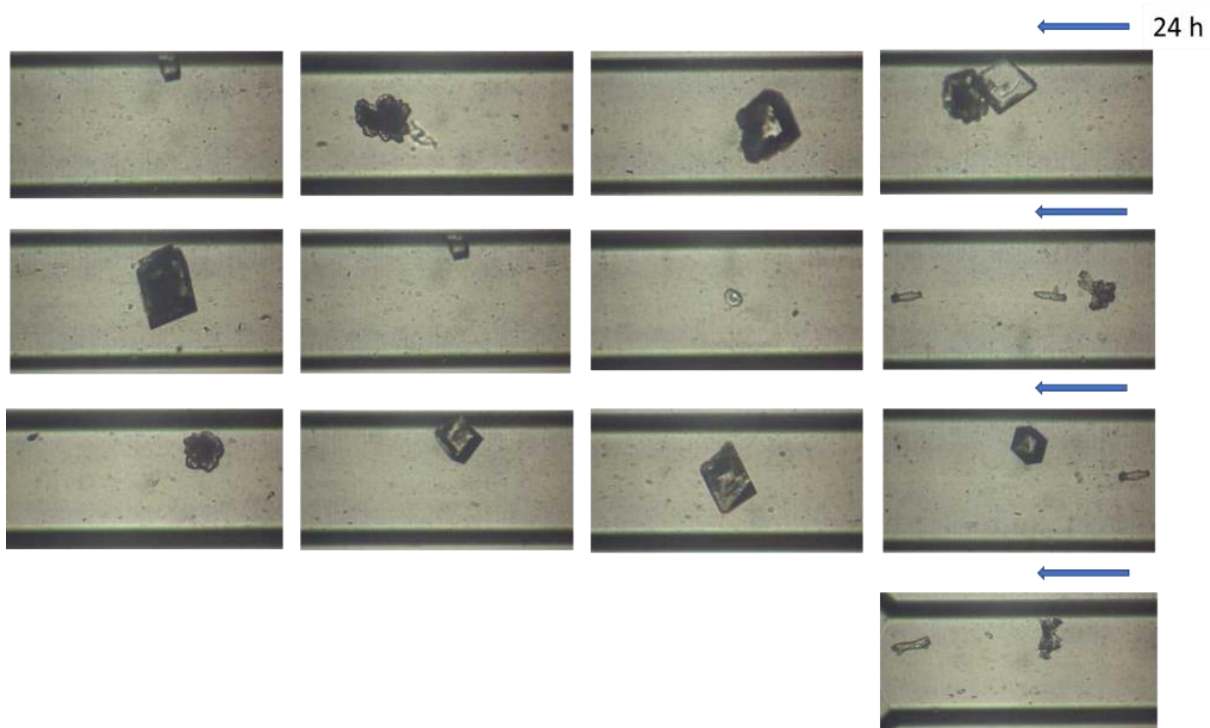

Figure 4: *CaCO₃ crystals formed during precipitation experiment at SR=30.2, along silane coated microchip in the presence of AOT (40 ppm), 24 hours from the start of the experiment.*

The presence of the cat-ionic surfactant (CTAB = 20 ppm) in both type of wettability accelerated the nucleation and the crystal growth of the first detected crystal compared to the experiments in the absence of surfactant [5]. Apart from the stable polymorph calcite, less stable polymorph such as aragonite was also detected (Figure 5).
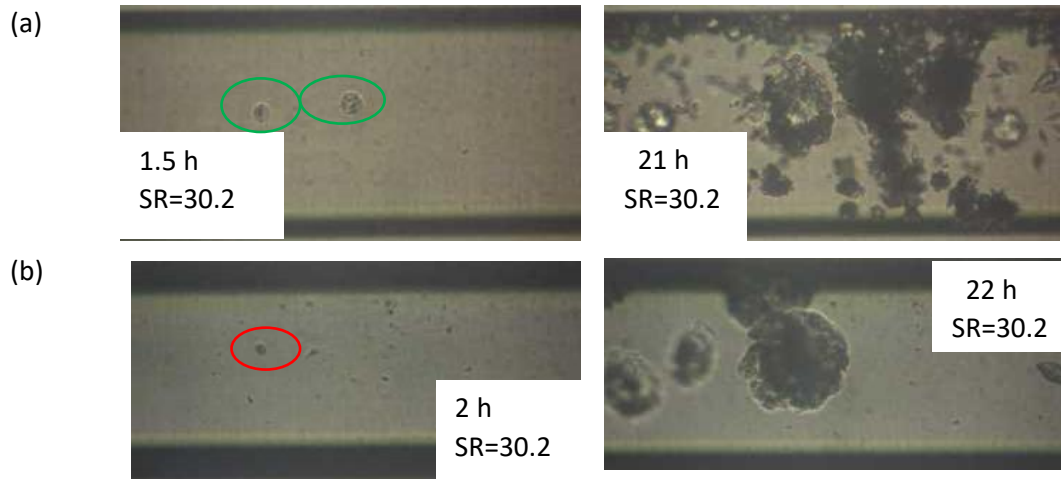
(a)

(b)

Figure 5: *Snapshots from the first observed crystals during CaCO₃ precipitation in (a) glass, (b) silane coated glass microchip in the presence of CTAB 20 ppm for SR = 30.2.*

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