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Influence of a multiphase system (organic and aqueous phases) on the calcium carbonate precipitation process

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Abstract

The literature lacks substantial works on the influence of multiphase systems on the calcium carbonate precipitation process, which is important for understanding this phenomenon in petroleum production. This work evaluates the calcium carbonate precipitation in a multiphase system composed of water and heptane at various ratios. The experiments were conducted in an automated batch reactor by mixing an aqueous phase containing 3290 mg L^{-1} of Ca^{2+} and 5000 mg L^{-1} of HCO_3^-, and an organic phase composed of an isomeric mixture of heptane. The experimental conditions were 25 ºC, pH 7, stirring of 1000 rpm for 60 min. The precipitation process was evaluated through FBRM and PVM, which showed the formation of heptane droplets covered with calcium carbonate solids and dispersed in the aqueous phase. This suggests that the calcium carbonate stabilizes the heptane droplets. SEM and XDR analysis of the calcium carbonate solids revealed a decrease in particle size with increasing heptane content. Moreover, the presence of the organic phase changed the typical morphology of calcium carbonate, increasing the proportion of the metastable crystalline phase vaterite. However, the experimental contitions studied did not allow determining the influence of the multiphase system on the precipitation kinetics.

Keywords

Scale; Calcium Carbonate; Multiphase

Introduction

Calcium carbonate scale is a significant flow assurance challenge in petroleum production. Despite employing various remediation and prevention methods, the petroleum industry has yet to find a definitive solution to this issue [1, 2]. The precipitation of calcium carbonate is one of the steps that leads to scale formation. Therefore, understanding this phenomenon is crucial, particularly in conditions similar to the real petroleum production scenario. Here, changes in thermodynamic parameters play a significant role in shaping the properties of calcium carbonate, including its crystal habit. Calcium carbonate solids can occur in various crystalline and amorphous phases [3]. Studying the conditions governing the formation of each solid structure is essential, given their impact on adhesion properties and thermodynamic stability that contribute to scale formation [4]. Several factors such as concentration, ionic strength, pH, temperature, and pressure, can influence the calcium carbonate precipitation process [5]. As petroleum is a multiphase fluid composed of hydrocarbons and water, the presence of an organic phase could also affect calcium carbonate precipitation. However, limited research exists on this topic, as most studies are conducted in single aqueous phase systems [6, 7]. This work investigates the influence of heptane, an organic phase, on the calcium carbonate precipitation process, examining the behavior of calcium carbonate solids within this multiphase system and changes in their morphology.

Methodology

Materials

Calcium chloride dihydrate and sodium bicarbonate were used to prepare the aqueous phase using ultrapure water. Heptane (Isomeric mixture) was used as organic phase. Sodium hydroxide, hydrochloric acid, and carbon dioxide were used to adjust the pH. The reagents were purchased from Isofar (Rio de Janeiro, Brazil) and used as received. The carbon dioxide was provided by Air Products (Rio de Janeiro, Brazil).

Precipitation experiments

The experimental setup consisted of an automated reactor Easymax® workstation Mettler Toledo (Columbus, USA), with temperature and stirring control. The precipitation experiments were conducted at 25 ºC, pH 7, using a total volume of 100 mL under mechanical stirring of 1000 rpm for 1 h.

The aqueous and organic phases were added to the reactor vessel at different ratios presented in Table 1. The aqueous phase was prepared by mixing two aqueous solutions of calcium chloride and sodium bicarbonate. The volume of each solution was calculated to achieve a final concentration of 3290 mg L^{-1} of Ca^{2+} and 5000 mg L^{-1} of HCO_3^-. A pH of 7 was adjusted by bubbling CO_2 into the sodium bicarbonate solution and by adding HCl 0.1 mol L^{-1} or NaOH 0.1 mol L^{-1} to the calcium chloride solution.

Table 1. Water:Heptane ratios and volumes used in each experiment

Heptane %(v/v)	Water volume (mL)	Heptane volume (mL)
0	100	0
5	95	5
10	90	10
25	75	25
50	50	50
75	25	75
90	10	90

To control the onset of precipitation, the aqueous solutions were added to the reactor vessel separately interspersed with the heptane. These additions sequence ensured that the precipitation occurred at the desired experimental conditions. The precipitation of calcium carbonate is given by the reactions presented in Eq. (1) and (2).

$$HCO^-_{3(aq)} + H_2O \rightleftharpoons CO^{2-}_{3(aq)} + H_3O^+_{(aq)} \quad (1)$$

$$CO^{2-}_{3(aq)} + Ca^{2+}_{(aq)} \longrightarrow CaCO_{3(s)} \quad (2)$$

At the end of each experiment, the reactor content was vacuum filtered through a 0.45µm MF-Millipore filter membrane. The filtered calcium carbonate solids were washed with ethanol, dried at 60°C for 10 min, and weighed. These solids were later analyzed by Scanning Electron Microscopy (SEM) and X-Ray diffraction (XDR).

Evaluation of the precipitation process

The calcium carbonate precipitation process was evaluated using Focused Beam Reflectance Measurement (FBRM) and Particle Vision Measurement (PVM), both from Mettler Toledo (Columbus, USA). The FBRM determines the particles' chord length distribution and particle count. The PVM acquires microscopic images of the calcium carbonate solids and the droplets formed in the multiphase system.

Results and Discussion

The amount of calcium carbonate solids obtained at the end of the experiments decreased with the increase of heptane content because the concentration of Ca^{2+} and HCO_3^- was fixed in the aqueous phase. However, the yield of the reaction was approximately equal for all the experiments, giving an overall yield of 23.3 ± 0.3 %. Figure 1 presents the yield of precipitated calcium carbonate for the different amount of heptane present in the mixture, showing that it did not influence the equilibrium and the relative amount of solids precipitated. The overall concentration of precipitated calcium carbonate was 1.91 ± 0.03 g per liter of aqueous phase present in the experiment.

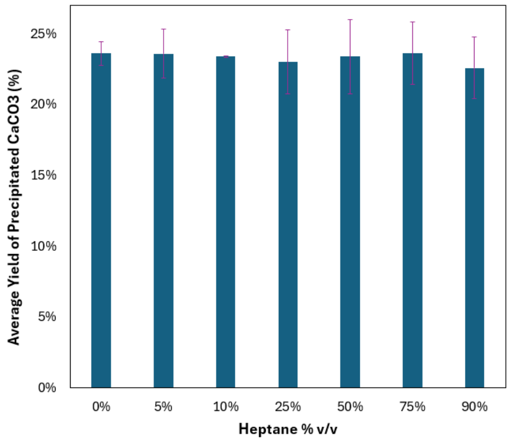

Figure 1. Yield of the precipitated calcium carbonate as a function of the relative volume of heptane phase present

Figure 2 displays the FBRM results for particle count (i.e. how many particles were formed over time) in the range of 10-50 µm. The data were treated to take into consideration the volume of the aqueous phase. This normalization treatment was performed since the amount of solids was dependent on how much aqueous phase was present in the experiment, as shown previously, which would then influence the FBRM signal.

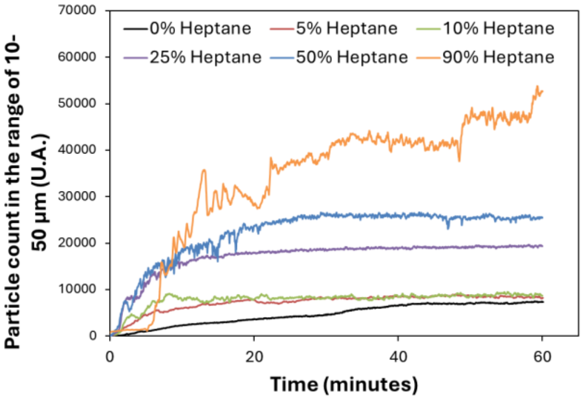

Figure 2. FBRM results of the particle count over time for particles in the range of 10-50 µm

It can be seen that by normalizing the signal to get the particle counts over the volume of water, the relative amount indicated that more particles in the 10-50 µm range was formed as the heptane content increased. This means that the presence of heptane led to a greater amount of small crystals. Since the relative mass of precipitated solid was almost constant for all experiments, this means that the experiments with higher heptane content led to an accumulation of this smaller particles, over the bigger particles. This can be seen in Figure 3, which shows the ratio of particle counts measured by FBRM at the end of the experiments. Figure 3(a) shows the ratio between the particles under 10 µm and the particles in the range of 10-50 µm, while Figure 3(b) shows the ratio between the particles under 50 µm and the particles in the range of 50-150 µm.

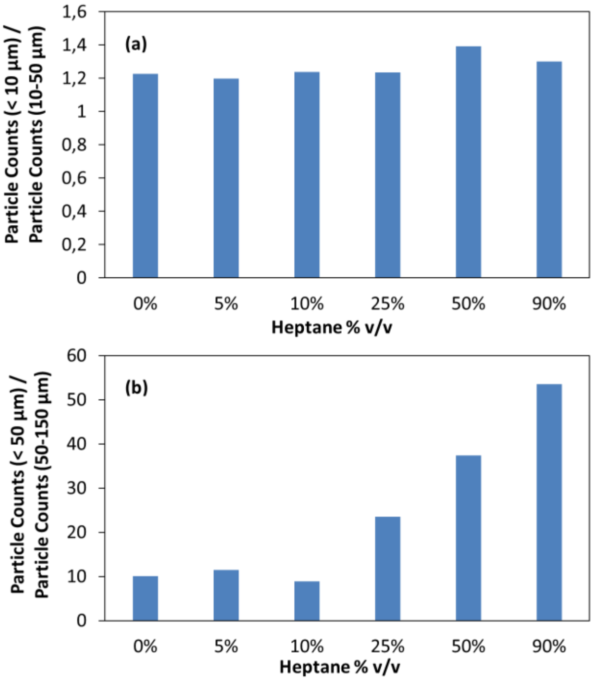

Figure 3. Ratio of particle counts of different sizes. (a) particles under 10 µm and particles in the range of 10-50 µm, and (b) particles under 50 µm and particles in the range of 50-150 µm

When comparing the counts of particles smaller than 10 µm and in the range of 10-50 µm, it can be seen that the ratio did not vary significantly for any content of heptane. However, comparing these smaller particles to larger particles (in the range of 50-150 µm), contents over 25% of heptane showed an increase in the ratio. This means that more smaller particles were produced in comparison to larger particles.

It should be noted that, although the FBRM could measure the droplets formed due to the stirring of the mixture, the signal did not show significant variation for any of the experiments using different heptane content. Hence, the signal measured by the FBRM can be related to the precipitation process itself.

Figure 4 displays the PVM results. The images show white objects that are the calcium carbonate particles, whereas the spheric structures observed in Fig. 4(b) are the heptane droplets. Moreover, the white particles in Fig. 4(b) seem to be interacting with the droplets, creating a coating-like layer at their surface.

Figure 5 shows the photos of the multiphase system reactor at the end of the experiments (after 1h). The presence of droplets even without stirring suggests that the coating-like layer of calcium carbonate stabilizes the heptane droplets in both the aqueous phase bulk and the interface.

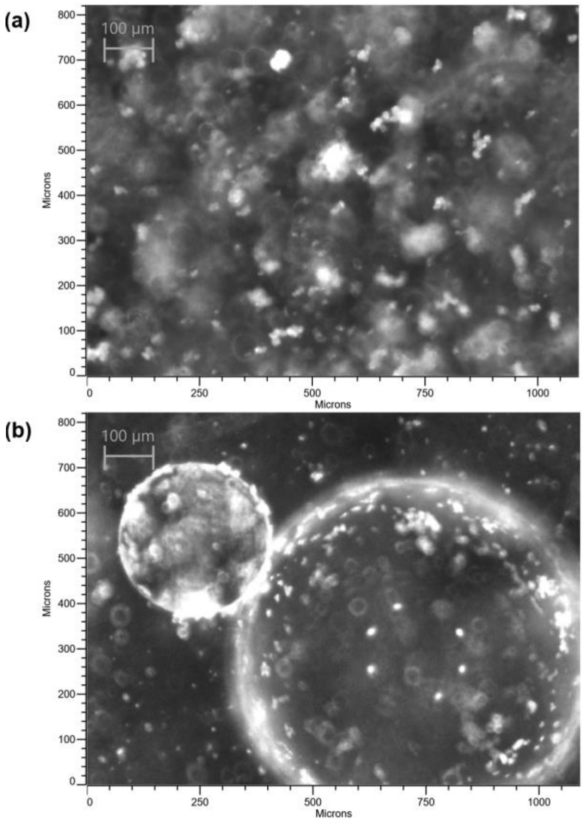

Figure 4. PVM results. (a) Heptane 0% and (b) Heptane 25 %.

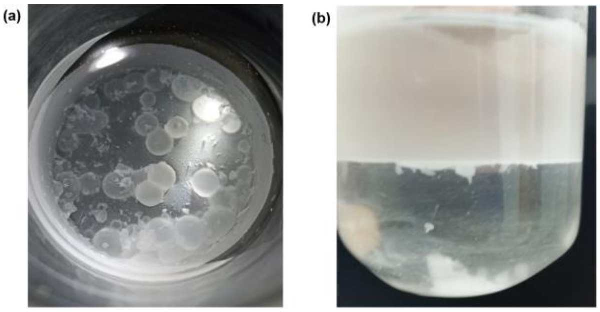

Figure 5. Photos of the multiphase system reactor at the end of the experiments. (a) Superior view and (b) side view of the reactor vessel

Figure 6 displays the SEM images of the calcium carbonate solids, which exhibited typical calcite and vaterite morphologies. Moreover, it can be observed the decrease in the particle size and agglomerates with the increase in heptane content, as was seen by the FBRM results. This suggests that the interaction of the calcium carbonate solids with the heptane droplets to form the coating-like layer affected their crystal growth and agglomeration processes. The decrease in particle size may also be related to the decreasing amount aqueous phase in the reactor, which affected the availability of ions during the dispersion of the water droplets in the heptane phase (or vice-versa). This may affect the crystal growth phase, together with the stabilization of the solid in the heptane-water coating surface.

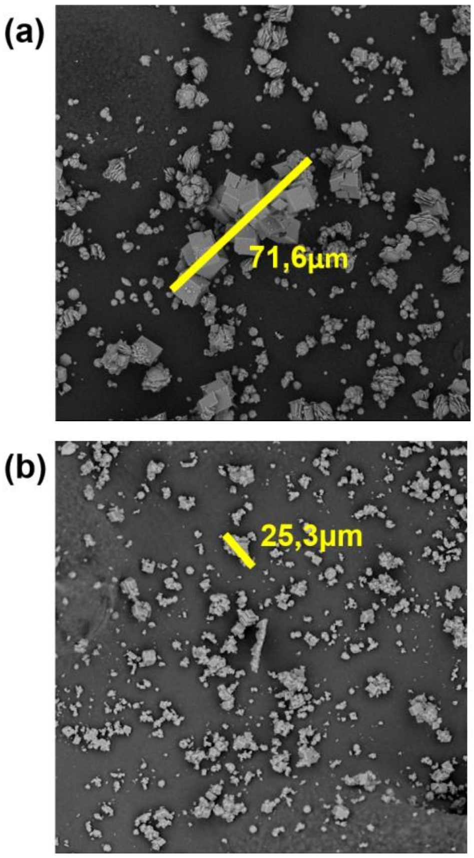

Figure 6. SEM images of the calcium carbonate solids obtained at the same magnification (1000X). (a) Heptane 0% and (b) Heptane 25%

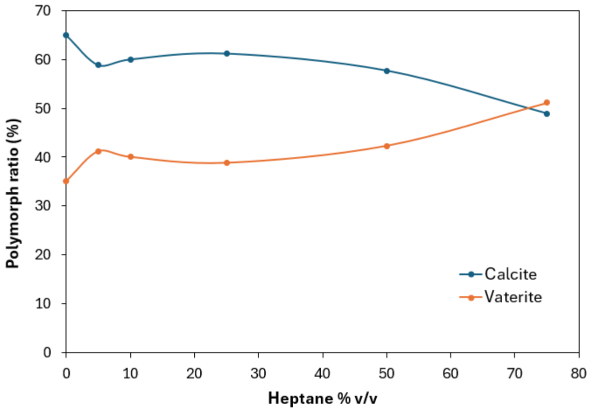

Figure 7. Vaterite and Calcite ratio obtained from the Rietveld refinement of the XRD patterns.

The XRD analysis confirmed the presence of the observed crystalline phases, calcite and vaterite. Moreover, the semiquantitative ratio between these phases was determined through a Rietveld refinement of the diffraction patterns. Figure 7 shows the results in which the increase in heptane content promoted the increase in the proportion of vaterite and the consequent decrease in the proportion of calcite. This suggests that the presence of an organic phase influences the stabilization of the calcium carbonate crystalline phases. Particularly, the increase of heptane content favored the metastable phase vaterite. This result can be related to the previous observations on the influence of the organic phase on the crystal growth and agglomeration stages.

Conclusions

A multiphase system composed of water and heptane influenced various stages of the calcium carbonate precipitation process. Increasing heptane content influenced crystal growth and stabilized the vaterite polymorph phase. This is probably due to the formation of a coating-like layer of the calcium carbonate solids that stabilized the heptane droplets in both aqueous phase bulk and interface. Even though the experiments were conducted at lower temperatures than that found during production, these findings contribute to the understanding the calcium carbonate precipitation process in petroleum production, offering insights for addressing flow assurance challenges associated with scale formation.

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