



Scanning Electron Microscopy investigations of hydrates and emulsions

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Abstract

Scanning electron microscopy (SEM) was utilized to analyze the morphology, texture, and structural evolution of hydrates and emulsions synthesized in the laboratory. Hydrates were synthesized under low-temperature and high-pressure conditions, originating from rounded droplets of water suspended in crude oil. Our observations revealed the presence of potential hydrates with geometric disk shapes, along with an increase in the thickness and roughness of the droplet interfaces.

Keywords

Scanning Electron Microscopy; emulsion; hydrate; high pressure; rheology.

Introduction

The crude oil industry's interest in fluids rheology is increasing throughout the years. Then, improved and more reliable methods for careful determination of composition, grain morphology, phase distribution, and microscopy of gas-hydrate are of great need. Methods such as nuclear magnetic resonance [1], X-ray tomography [2, 3], and magnetic resonance microimaging (MRM) [4, 5] have demonstrated their utility as non-invasive imaging tools for observing hydrate formation [6]. Another interesting technique for gaining further insights into hydrate growth processes is scanning electron microscopy (SEM) [6]. Cryogenic systems are usually integrated into the SEM to allow visualization of fluid systems, and are being used predominantly for biological and food applications. The system facilitates the successful imaging of clathrates and other icy compounds. Nonetheless, the utilization of this technique for imaging gas hydrates has only recently emerged in the literature in the early 2000's [6]. Several studies have used cryo-SEM imaging to identify grain structures with different types of gases [6-10]. Furthermore, there have been reports of fully dense crystals, with nonporous and mesoporous surface texture [7,8].

Here, we apply SEM techniques to observe grain, surface and pore structure development associated with gas hydrate formation from the reaction of a hydrate-forming gas and water droplets dispersed in crude oil. We first show images of emulsions with and without salt. We measured the size and distribution of these droplets and looked inside them to observe the distribution of salt crystals with and without hydrate formation. Synthesized gas hydrates at high

pressure and low temperature were analyzed, observing changes in thickness and rugosity on the droplet surface. Also, some hydrate crystal shapes formed at the interface of the droplets were successfully observed.

Methodology

This section describes the methodology for obtaining both an emulsion and a hydrate, and detail the experimental procedure for cryo-SEM measurements. The protocols of preconditioning of crude oil and emulsion preparation follow a protocol suggested by CENPES/Petrobras.

Materials

The crude oil was given by CENPES/Petrobras and presented 0.4% of water content and 29.3 °API. Tab. 1 shows the composition of the synthetic sea water.

Table 1. Composition of synthetic water

Salt	(g/L)
CaCl ₂	2,0
NaCl	55,0

Experimental Procedure

- **Preconditioning of crude oil**

The oil undergoes agitation using a mechanical stirrer atop the oven, rotating at 300 rpm for 3 hours at 80°C. This temperature surpasses the WAT (Wax Appearance Temperature) threshold. This ensures the complete dissolution of any crystals. Subsequently, the treated crude oil is transferred into 1-liter Schott glass bottles and stored at 25°C.

- **Emulsion preparation**

All experiments were conducted with a 50/50 volumetric ratio of water and crude oil. The crude oil from the preceding step undergoes heating in an 80°C oven for 1 hour before being transferred to a 500 mL bottle. Water is then added under manual agitation. Subsequently, the emulsion is stirred using a Turrax (manufactured by IKA) for 3 minutes at 8000 rpm.

- **Bulk rheology at high pressure**

We employed the Haake Mars III rheometer with Vane geometry and a pressure cell to measure bulk rheology. The emulsion was introduced into the pressure cell, initiating the experiment at 60°C and pressure of 150 bar, with a shear rate of 50s⁻¹. Throughout the experiment, the pressure within the cell was kept constant. Following an hour of gas incorporation at 60°C, the temperature gradually decreased to 4°C at a cooling rate of 0.8°C per minute. Viscosity measurements were continuously recorded to track hydrate formation at this specific temperature.

- **SEM imaging procedure**

Each sample underwent immersion in liquid nitrogen, ensuring the rapid freezing of a small section for analysis. Subsequently, samples were fastly transferred to a sample stage within a pre-chilled (-140°C) Quorum cryo-preparation chamber, which was connected to the TESCAN Clara field emission SEM. Within the preparation chamber, the section was fractured using a cold blade to uncontaminated surfaces for imaging, free from surface condensation. In some cases, samples were coated with Pd for 60 seconds using a sputter head. Then, they were directly inserted through the back of the preparation chamber onto an auxiliary cryo-imaging stage within the SEM column. Imaging took place at temperatures below -170 °C, employing low voltage (≤2 kV) to minimize sample alteration or beam damage to the surface.

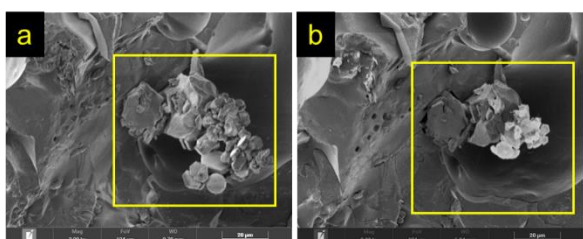


Figure 1. Micrographs of hydrate crystal with disk shape a) in the first time of scanning analysis, b) after a long time of exposition to the beam current. Damage in the microstructure is observed after prolonged exposition to the beam current.

Multiple areas were imaged both initially (Fig. 1a) and subsequently during each session to track changes in surface topology over time (Fig. 1b), a standard procedure in our SEM imaging of hydrates. However, phase identification remains challenging in certain cases. When cryo-SEM is

applied to gas hydrates, we must have some additional technical care present, such as preventing atmospheric water condensation on samples during cold transfer, applying an electrically conductive coating, without causing heat or damage to the sample surface, and ensuring that the hydrate sample remains under conditions that prevent spontaneous decomposition or significant sublimation under vacuum, and also preventing electron beam damage to the imaging area.

Results and Discussion

Figure 2 illustrates the dispersion of water droplets within the crude oil bulk. Droplets ranging in size from 5µm to 50µm are observed. The images provide a comprehensive visual representation of emulsions created using deionized water (Figs. 1a and 2b), emulsions formed with synthetic water before undergoing rheometer testing (Figs. 1c and 1d), and emulsions observed after the high-pressure rheology test (Figs. 1e and 1f). As anticipated, upon sublimation of the water, salt crystals were discernible within these droplets. A distinct and organized structure was identified within these salt crystals following the rheology test, potentially indicative of hydrate or ice formation at the interfaces of these droplets.

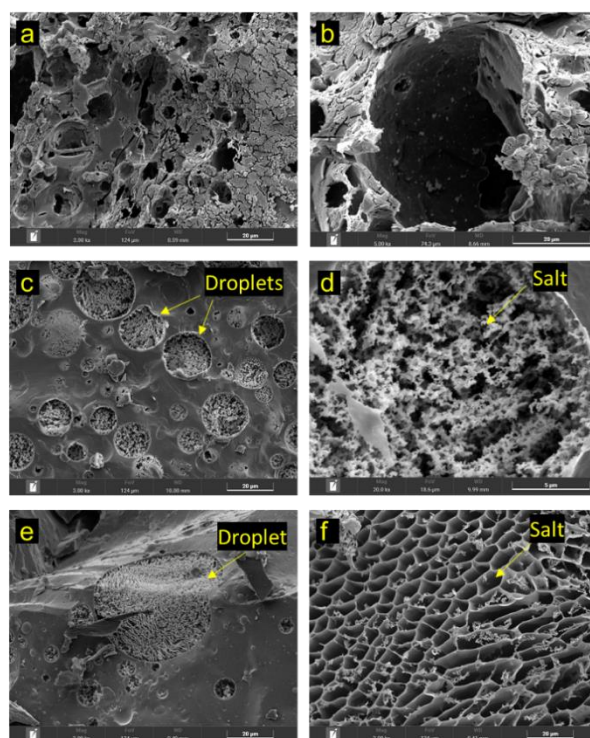


Figure 2. Micrographs of an emulsion of synthetic water and crude oil 50% v/v a) without salt, b) with salt, and c) salt crystal organized. Images b), d), and f) are zooms of one droplet of the respective left image.

Figure 3 depicts the alterations in droplet thickness and roughness upon hydrate formation. This observation aligns with previous research

indicating that hydrate formation initiates at the water/crude oil interface, gradually augmenting droplet thickness until the gas contact with the water is impeded by the hydrate itself, thereby halting the hydrate formation [11].

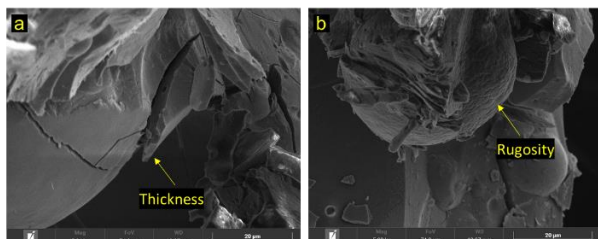


Figure 3. Micrographs of droplets surfaces of an emulsion of synthetic water and crude oil 50% v/v. Highlight the increase of a) thickness and b) the rugosity of the shell.

Figure 4 presents a micrograph of a disk-shaped crystal exhibiting six faces. This crystal was discovered within the shell of one droplet, precisely where we anticipated finding it, as hydrate formation occurs at the interface between water and crude oil [12]. However, this disk-shaped hydrate is uncommon in articles utilizing the same technique. Some articles suggest the possibility of it being hydrohalite ($\text{NaCl}\cdot 2\text{H}_2\text{O}$) or a simple disk crystal of ice [13]. Another notable point is that this disk can be considered as a starting point (or nucleus) for hydrate growth to the formation of sII methane-ethane hydrate [7]. This represents our initial attempt to develop an experimental procedure that allows us to obtain more conclusive results and micrographs of grains with shapes and surfaces more closely resembling those suggested in the literature [6].

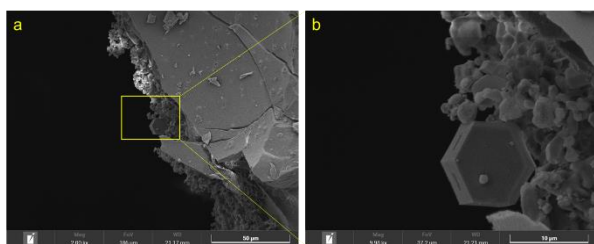


Figure 4. a) Micrographs of hydrate cage in the emulsion shell, and b) zoom of the image highlight the disk shape of the hydrate.

Conclusions

This work presents a preliminary attempt to develop an experimental methodology for obtaining the hydrate structure under sample preparation conditions using cryogenic systems, followed by sample analysis in the SEM. As preliminary results, we were able to visualize the emulsion and gain an understanding of the size and distribution of the droplets. Additionally, we identified salt crystals within the water droplets and observed how these crystals organized themselves in an orderly manner when subjected to high pressures and low temperatures. We

observed the presence of disk-shaped crystals at various points in the sample, especially at the water/oil interface, which suggest the possibility of them being hydrates or nuclei for the formation of structures closer to type sII. We also noted an increase in the roughness and thickness of the droplet interfaces, possibly associated with the formation of hydrate shells around them.

Acknowledgments

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Responsibility Notice

The authors are the only ones responsible for the paper content.

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