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High-pressure liquid-liquid equilibria for high gas content on pre-salt samples

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Abstract

Understanding the competing phases of fluid flow through a porous medium is an important step for reservoir engineers. Nevertheless, this is still a complex task because of the diversity of compounds in reservoir fluids. In the last decades, different phase transition methods and tools have been developed to detect phase transitions better and reduce the uncertainties related to reservoir engineering, e.g., NIR light scattering, high-pressure microscopy, acoustic techniques such as quartz crystal resonators, and non-visual wavelength imaging. Using these new techniques brings phase behavior challenges, such as high-temperature and high-gas content liquid-liquid equilibria (HTLLE), characterized by its high dispersity, no fractal structure, non-coalescence, and rapid redissolution. This unexpected phase transition was first recorded in the literature in 2015, and the oil industry has yet to be fully included in the reservoir simulation workflow. This work summarized the main findings from 5 (five) different Brazilian crude oils, including recombined and live oil samples, classical pressure-volume curve, Y-function curve, high-pressure microscopy, and full visual techniques.

Keywords

High Gas Content; Fluid Phase Behavior; Second Liquid Phase

Introduction

Pressure, temperature, and composition variations during the production of reservoir fluids are frequently related to complex fluid phase transitions, leading to changes in fluid properties and multiphase flow. For this reason, a full understanding of the phase behavior of reservoir fluids is a determining point for designing, optimizing, and modeling oil production [1] with lower uncertainties. It is well known by oil industries that carbon dioxide (CO_2) is used as a solvent for the Enhanced Oil Recovery (EOR) process due to its solubility in crude oil at reservoir operational conditions and understanding its effects on oil properties is fundamental for planning oil recovery processes [2]. This work is part of a series of studies that aims to understand the high-temperature liquid-liquid equilibrium in different Brazilian pre-salt crude oil to understand the phase equilibria observed in such systems and, mainly, the nature of dispersed phase formed. The main objective of this paper is to investigate the fluid phase equilibria of different opaque Brazilian pre-salt crude oil-CO_2 systems at different temperatures and pressures up to 100 MPa and to provide valuable experimental data and analysis to enhance the understanding of the system's phase behavior.

Methodology

A variable volume high-pressure PVT cell was used to prepare high-carbon dioxide mixtures for pressure up to 100.00 MPa and temperature up to 473.15 K. Additionally, this PVT cell is coupled with and a high-pressure microscope comprising an external high-pressure cell with two sapphire windows separated by 100 μm. Phase equilibria determination for high opacity crude oil samples is challenging because of the difficulty of fluid phase boundary determination, especially for fluid-fluid transitions such as liquid-liquid and liquid-liquid-vapor. For this reason, a Short-Wave Infrared (SWIR) camera and light source were integrated into the HPM. This architecture provides accuracy in observing and determining complex phase boundaries, once using a horizontally oriented high-pressure cylinder, ensuring full fluid sample visibility. The cylindrical vessel's chamber has an inner diameter of 16 mm and a maximum volume of 30 cm^3. A movable piston, actuated by an electric step motor, is on the opposite side of the sapphire window. Precise control over the sample's volume and pressure is achieved through controlled upward and backward piston movements using virtual instrument control software. Thermal regulation is accomplished by circulating a heat carrier liquid within a thermal jacket covering the entire cell body. A high-precision thermostatic bath propels the heat carrier fluid with a temperature stability of ±0.02 K. A

Pt100 probe measures the system's temperature in a blind hole on the jacket's wall, positioned as close as possible to the sapphire window. Additionally, fluid temperature is measured by a thermocouple directly placed inside the chamber to validate thermal equilibrium with the system temperature.

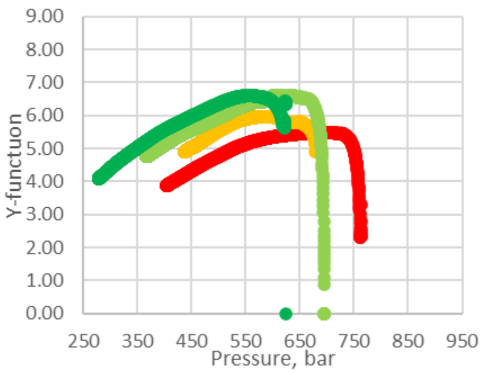
All experimental phase transitions were determined by performing a controlled depletion with a mid-ramp equilibration step. The pressure system was increased until the system reached a monophasic liquid state, or two liquid phases were observed in equilibrium. A combination of indirect and direct techniques was used to determine phase transitions. For instance, the pressure-volume curve was used to determine the traditional bubble point mixture at a fixed temperature. However, the plot of the volume against pressure was used for a mixture with high gas content. The pressure-volume curve and the Y-factor results are integrated with the visual SWIR inspections to verify the medium's non-uniformity caused by a phase transition in the bulk fluid.

Results and Discussion

Two different crude oil samples are investigated, named as, PrS and PrS1 by adding different gases. PV curves could not describe the bubble point transition in a high gas content condition [1], as given in Figure 1 to PrS + synthetic gas (z_{gas} = 75 mol %), been synthetic gas by an equimolar 1:1 mixture of CH_4 and CO_2. This behavior could be attributed to higher gas compositions, leading the system to near-critical fluid behavior. Moreover, the continuous shape can suggest a slow phase formation at conditions just below the transition pressure [2].

The trend line intercepts on Y-function bubble point pressure determination were carried out using a visual analysis, i.e., the liquid phase trend line was fitted for a region before a visual identification of a gas-liquid interface, as shown in Figure 1. Nevertheless, for the high gas content sample, it was not possible to determine bubble point transition once the PV and Y-function curves were strongly straight. For this reason the SWIR-HPM architecture was used [2,3].

(A)



(B)

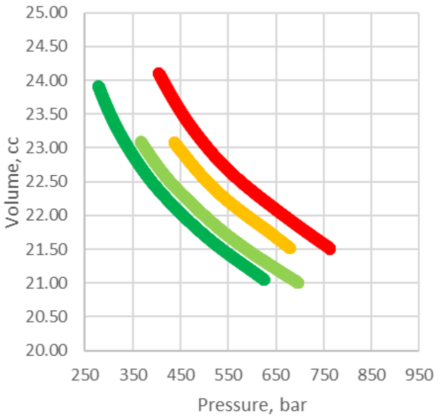


Figure 1. PrS + synthetic gas (z_{gas} = 75 mol %) constant composition expansion. (A): Y-function. (B): pressure-volume curves: 50 °C (●), 65 °C (●), 85 °C (●), and 105 °C (●). synthetic gas (50 mol% CH_4 + 50 mol% CO_2)

Figure 2 shows different phase equilibria observed for PrS1 by adding CO_2 at T = 94 ºC. Figure 2(A) presents a classical bubble point for a mixture with low gas content where a vapor phase can be observed in equilibrium with a continuous liquid oil phase. Otherwise, Figure 2(B) depicts a dispersed liquid-liquid equilibrium (LLE) observed in a PrS1+ CO_2 sample. This LLE is characterized by a demix of a denser and viscous liquid phase, which does not present a segregation behavior by gravity, suggesting that the liquid phase shows a low-density contrast. Interestingly, LLE does not show any variation in fluid compressibility.

Nevertheless, as fluid depletion evolves inside the HPM, a bubble point is observed, and the tiny drops regarding the dispersed LLE remain in equilibrium, showing how complex the fluid phase transitions could be in pre-salt reservoir fluids. In this example, a dispersed LLE evolves to a three-phase liquid-liquid-vapor equilibrium at high pressure and high-temperature conditions, as shown in Figure 2(C). Figure 2(D) illustrates an asphaltene-liquid-liquid equilibrium at high-pressure conditions, where the asphaltic phase prefers to be adhered to the polar surface of the sapphire windows [4]. Moreover, it is possible to observe that the second liquid phase prefers to interact with the asphaltic phase. In summary, the second phase formation can be attributed to the high gas content condition and the high asymmetry between the heavy hydrocarbon fraction in the PrS1 sample and the gas, presenting a significant difference in their molecular size and properties.

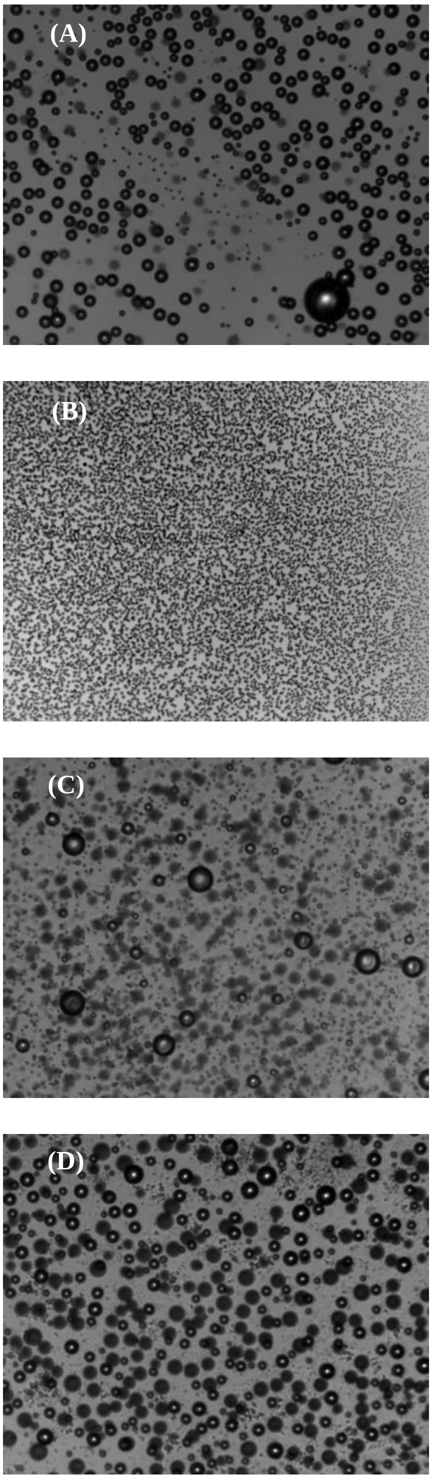


Figure 2. Fluid phase behavior analysis using SWIR-HPM architecture for a PrS1 + CO_2 at different global compositions at T = 94 ºC. (A): vapor-liquid equilibrium for mixture with 50 mol% gas; (B): liquid-liquid equilibrium for mixture with 75 mol% gas; (C): liquid-liquid-vapor equilibrium for mixture with 75 mol% gas; and (D): solid-liquid-liquid equilibrium for mixture with 80 mol% gas.

When the same crude oil present in Figure 2 was studied in a high-CO_2 content (above 80% molar) condition and T = 60 °C was studied using a full visibility cell, it was possible to observe a barotropic phenomenon, as depicted in Figure 3. In Figure 3(A), the high-density liquid phase is observed at the bottom of the cell. Otherwise, as pressure decreases, the liquid phase is observed at the top of the cell, as shown in Figure 3(B). This phase inversion could be attributed to (i) high compressibility and (ii) high density of the second liquid phase. Although such a high CO_2 composition is not typical in regular reservoirs, it could be reached during the CO_2 injection process. The impact of the barotropic inversion is not well evaluated from a production and elevation point of view; for the authors, it could be attributed as an important uncertainty for reservoir assessment and engineering.

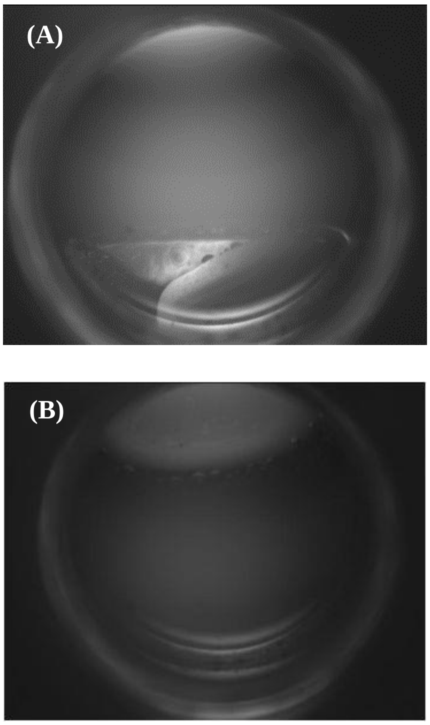


Figure 3. Barotropic inversion for PrS1 + CO_2 system at T = 60 °C and pressure from 630 bar to p = 550 bar.

Conclusions

The incoming conclusion relies upon three main factors determining the occurrence of high-temperature and high-gas content liquid-liquid equilibria (HTLLE): gas (methane and carbon dioxide) and heavy petroleum compounds asymmetry; gas phase density and compressibility; and high gas content. Nevertheless, more studies are still necessary regarding pre-salt samples' fluid phase equilibria and their impact on oil and gas production.

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Responsibility Notice

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