

Phase behavior and viscosity of CO₂ rich fluids with low content of gas condensate

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Abstract

Carbon dioxide (CO₂) is considered the most significant greenhouse gas produced by human activities. The primary goal of humanity is to manage the CO₂ in a way that minimizes its impact on our atmosphere. One intuitive approach to dealing with CO₂ is to inject and store it in subsurface formations, a practice commonly employed by petroleum companies for enhanced oil recovery. Despite being as dense as water under high-pressure conditions, CO₂ exhibits atypical flow behavior due to its lower viscosity. Therefore, understanding the properties of CO₂-dominant mixtures, especially those containing hydrocarbons, is crucial considering the actual scenario of energy transition. In this study, we investigate bubble/dew points and viscosities of CO₂ mixtures with low content of a well-characterized gas condensate. It was found that dew point pressures increase sharply with gas condensate fraction increase. For the viscosity characterization, it was found that the viscosity increase as pressure increases.

Keywords

CO₂; Gas Condensate; Phase Behavior; High Pressure Viscosity

Introduction

The atmospheric release of carbon dioxide has emerged as an environmental concern, particularly with regard to its role in global warming. This issue is further compounded by the high concentration of CO_2 found in the majority of Brazilian pre-salt reservoirs, necessitating the implementation of effective disposal measures ^[1].

One such solution, which offers both environmental and operational advantages, involves the reinjection of CO_2 back into these reservoirs ^[2]. Not only does this practice aid in maintaining reservoir pressure, but it also facilitates enhanced oil recovery, contributing to the optimization of extraction processes as a whole.

However, while efforts are made to separate CO_2 from hydrocarbons for utilization in energy production and commercial ventures, a complete and economically feasible segregation remains impossible. Consequently, the injection stream comprises not only CO_2 but also residual natural gas and other impurities.

Hence, recognizing the significant impact that even minor quantities of hydrocarbons can have on the dynamics of a CO₂-rich flow stream, it becomes imperative to delve into the properties of this blend, particularly focusing on phase behavior and viscosity. This paper shows phase behavior and viscosity data for mixtures containing CO₂ plus a low concentration of a model gas condensate.

Methodology

A Schlumberger PVT apparatus was used to evaluate compressibility factor (density), phase transitions and condensate volume (using a conical piston) of known composition mixtures.

The other equipment used in this work was a highpressure viscometer Cambridge VISCOlab PVT, Cambridge Viscosity for obtaining the viscosities of the model fluids.

The first step of the work was to characterize a gas condensate fluid which has a similar composition from the gas condensate proposed in a paper of the literature ^[3]. This mixture was added in low concentration to pure CO₂, and this blend was characterized in this study.

PVT Visual Cell

The Schlumberger Visual PVT Cell used in this study is suitable for characterizing the phase behavior of fluids under different temperature and pressure conditions. The maximum working volume is 80 cm³, limited to extreme operational conditions of 100 MPa and -10 to 180°C. Capable of monitoring and inducing Pressure, Volume, and Temperature variations, it is used, among other

functions, for determining bubble and dew points, identifying the retrograde condensation region of hydrocarbons, and measuring specific masses as a function of pressure and temperature. The main components of the Visual PVT Cell are presented below:

- (a) steel jacket;
- (b) air bath surrounding the steel jacket;
- (c) positive displacement pump;
- (d) set with cathetometer and camera;
- (e) floating-piston cylinder for sample injection;
- (f) floating-piston cylinder for gas injection.





The fluid volume within the visual cell is crucial for PVT analysis and properties determination. Three factors are considered for quantifying the sample volume and volume changes in the system: the sample height inside the cylinder, obtained through level indicator readings located by the camera displacement in the cathetometer; the crosssectional area of the cylinder; and the dead volume of the section between the sample supply valve in the cell and the entry into the cylinder.

Experimental Procedure

The fluid sample is initially contained in a highpressure steel cylinder with a floating piston. It is pressurized by an auxiliary high-pressure pump injecting the hydraulic fluid. The sample-side of the cylinder is connected to the visual PVT cell. The pressure in this high-pressure cylinder, which is the desired value for injection procedure, must remain slightly above the pressure in the PVT cell (around 200 psi) to direct the cylinder flow into the cell, thus preventing reverse flow.

The volume of the sample to be injected is previously calculated, considering fluid expansion due to temperature increase and pressure reduction, as well as new gas injections.

Before injecting the fluids, a vacuum pump is used to avoid air contamination. For the injection procedure, all valves between the steel cylinder and the entry into the visual cell must be opened. Thus, the sample is driven towards the cell as the hydraulic fluid (water) is injected into the cylinder. The equilibrium cell receives the sample through the lower head where there is an inlet port, and the sample will accumulate at the bottom of the glass cylinder below the piston, which is pushed upward as the sample enters in the cell. At the end of filling, the volume inside the cell is recorded and used as a reference for calculating the density.

Constant Composition Expansion

Constant composition expansion is a test based on expanding the fluid contained in the visual equilibrium cell while maintaining its composition constant, without removing any phase formed during depressurization. The test begins at pressures higher than the saturation pressures and continues until pressures below the saturation pressure (bubble or dew pressure). Each test can provide the following results: sample saturation pressure (bubble pressure or dew pressure); relative volume (ratio of the volume the fluid occupies at any pressure to the volume occupied at saturation pressure); volume of liquid and/or gas phases at the measured pressure and saturation pressure; and the density of the sample above the saturation pressure (one phase).

Composition of the Mixture

The molar composition of the gas condensate is 80.096 CH₄; 13.921% n-C₄H₁₀; 3.992% n-C₇H₁₆; 1.393% n-C₁₀H₂₂; 0.59680% n-C₁₄H₃₀ and its pressure-temperature (PT) plot for bubble and dew points of this mixture in shown in Fig. (2).





This synthetic mixture has density of 0.4063 g/cm³ (measured with a high-pressure pycnometer). The resultant molar mass of the mixture is 28.11 g/gmol according to the composition. At 20 °C the phase transition is bubble point while at the higher measured temperatures it is dew point. This hydrocarbon mixture was combined with CO₂ in the PVT cell as follows: (Mixture 1) 3.3% gas mixture and 96.7% CO₂ and (Mixture 2) 5% gas mixture and 95% CO₂ for the PVT studies. The

table below shows the global composition of these mixtures.

Components	Mixture 1	Mixture 2
Methane (CH ₄)	0.0262	0.04
Butane (C ₄ H ₁₀)	0.0045	0.0069
Heptane	0.0013	0.002
Decane	0.0005	0.0007
Tetradecane	0.0002	0.0003
CO ₂	0.9673	0.9501
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Table 1. Molar global composition of the mixtures

Source: elaborated by the author (2023)

High-Pressure Viscosity Measurements

The viscosities of the mixture CO_2 +gas condensate were measured at temperatures varying from 313 to 353 K and pressures above the saturation pressure of the mixture up to 35 MPa.

The samples were prepared adding known volumes of gas mixture to the CO_2 in a high-pressure cylinder obtaining the desired composition (95% de CO_2 , 4.0% of CH₄, 0.69% of C₄H₁₀, 0.20% of C₇H₁₆, 0.07% of C₁₀H₂₂ and 0.03% of C₁₄H₃₀).

Results and Discussion

The measurements in the CCE test were carried out at four temperatures (20 $^{\circ}$ C, 40 $^{\circ}$ C, 60 $^{\circ}$ C, and 80 $^{\circ}$ C) with a working pressure of 34.5 MPa (value considered for starting the isothermal depressurization). The graph in Fig. (3) illustrates the saturation points.



OPsat (3.3% Gas Mixture) ■Psat (5% Gas Mixture)

Figure 3. Bubble or dew pressure Source: elaborated by the author (2023)

In Fig. (3), there were two types of saturation pressure: bubble point at 20 °C and dew point for the higher temperatures.

The density of the overall system decreases with increasing temperature and increases with increasing pressure. The presence of the mixture of synthetic gases in the CO_2 caused a decrease in its density. The higher the CO_2 content of the gas mixture, the lower its density. As an example of the

data found here, the density of the undersaturated system containing 3.3% gas mixture at 20°C and 34.5 MPa is 0.9756 g/cm³, while the density of pure CO_2 under the same conditions is of 1.0016 g/cm³. The graphs in Fig. (4) and (5) respectively show the compressibility factor Z (directed related to specific mass) at different temperatures for 3.3% and 5% of gas mixture added to CO_2 .

For the same temperature, the compressibility factor is inversely proportional to the hydrocarbon content, that is, the more CO_2 in the system, the greater the compressibility. Regarding the behavior of this variable in relation to temperature variation, it is clear that higher temperatures display higher compressibility factors.



Higure 4. Compressibility factor 2 for 3.3% hydrocarbons together with CO₂ Source: elaborated by the author (2023)



Figure 5. Compressibility factor Z for 5% hydrocarbons together with CO₂ Source: elaborated by the author (2023) In addition to determining the phase transition (bubble or dew point), the volumes of liquid in relation to gas inside the cell - relative liquid volume - were obtained at some PT coordinates inside the phase envelope of Fig. (3). This experimental data is shown graphically in Figs. (6), (7), (8) and (9), which correspond, respectively, to the temperatures 20, 40, 60 and 80°C. As expected, the liquid volume at bubble pressure (20°C) is relatively larger than the liquid volume for the higher temperatures, where dew pressures were observed.

Analyzing the graphs in Fig. (7), (8) and (9), it is noticeable that the higher the content of the hydrocarbon mixture in the system with CO_2 , the greater the relative volume of condensed liquid at the same temperature analyzed. In addition, the data shows a slight reduction in the volume of condensed liquid as the test temperature increases.



















Regarding the high-pressure viscosity measurements, it is possible to conclude from Fig. (10) that, for the investigated pressures ranges, the gas condensate mixture reduces the viscosity of CO_2 . The data indicates that the higher the pressure, the greater the difference between the viscosities of pure CO_2 and the CO_2 mixture.



Figure 10. High-pressure viscosity measurements of pure CO₂ and a mixture of gas and CO₂ Source: elaborated by the author (2023)

Conclusions

The following conclusions can be draw from the results obtained in the present study:

- The density of the CO₂ subsaturated system and hydrocarbon mixture decreases with increasing content of the model gas mixture;
- Another observation is that these systems exhibit high dew point pressures and the difference between saturation pressures of 3.3% and 5% increases with temperature;
- For the range of pressure analyzed in this study, the presence of the gas condensate decreases the viscosity of the mixture. The difference in viscosity is higher as the pressure increase.

Responsibility Notice

The authors are the only responsible for the paper content.

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