



## Preparation and characterization of a high CO<sub>2</sub> content synthetic fluid

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### Abstract

In this paper the preparation and characterization of a synthetic sample of gas condensate-like fluid with high CO<sub>2</sub> content is described. Also, a mixture of CO<sub>2</sub> and CH<sub>4</sub> was produced for an interfacial tension testing with the dead oil sample. Using information of a reservoir fluid, a mixture of CO<sub>2</sub> and CH<sub>4</sub> was combined with dead oil in order to approach the original fluid. Thus, a synthetic reservoir fluid was approached using only CO<sub>2</sub>, CH<sub>4</sub> and a dead oil. The samples were analyzed in terms of constant composition expansion, constant volume depletion, gas-oil ratio, composition, density, molar mass, high and ambient pressure viscosity and high-pressure interfacial tension. During the depressurization in conditions below the dew point pressure, the density of the less dense phase showed a breaking point around 3000 PSIG where the compressibility starts to manifest pronouncedly. The viscosity of the dense gas is one order of magnitude lower than the water viscosity.

### Keywords

Synthetic recombination; high CO<sub>2</sub> content; high-pressure fluid behavior

### Introduction

Pre-salt carbonate reservoir fluids are likely to contain high fractions of carbon dioxide. The content varies, reaching ultra-high values. Such mixtures of hydrocarbons and CO<sub>2</sub> are not well reported in literature, and the results of simulations by equations of state are not reliable.

Therefore, experiments are needed in order to understand the behavior of such fluids [1]. Specifically, ultra-high CO<sub>2</sub> content systems (70%-98% mole) are relevant when dealing with CO<sub>2</sub> injection for carbon capture and storage (CCS) [2] and enhanced oil recovery [2,3]. Furthermore, knowledge on such type of phase behavior can be useful for high-pressure separator design [4].

Through phase behavior studies, the volumetric changes as a function of pressure are used in flow system design. Fitting equation of state, conceiving/fitting correlations and characterizing the flow behavior are one of the main concerns in the study of high-pressure fluid samples. Furthermore, the interfacial behavior is an important variable when dealing with phases of similar densities, which are common in CO<sub>2</sub> rich mixtures with hydrocarbons. In such a context, this paper reports a sample preparation and a PVT characterization. The phase behavior is discussed afterwards.

### Methodology

The following devices were used in this study.

Density: Anton Paar DMA 4500M. Molar mass: OSMOMAT 010. Composition: Agilent chromatograph. Dead oil viscosity: Capillary Cannon-Fenske viscosimeter. High-pressure viscosity: Cambridge viscosimeter VISCOpro 2000. Gas volume: Schlumberger Gasometer. Phase equilibrium experiments: PVT Schlumberger, High-pressure density: Pycnometer, Recombination: Piston cell, recombiner, and booster and Interfacial tension: high-pressure Kruss tensiometer (pendant drop).

### Experimental Procedure

The components of the synthetic fluid are CO<sub>2</sub>, CH<sub>4</sub> and a light oil (°API 35). The dead oil was characterized by viscosity, density, and molar mass. Then, the fluids were introduced in the piston cell and maintained under agitation for two days at 9000 PSIG. Then, the undersaturated fluid was transferred from this high-pressure cylinder to a PVT visual cell at constant pressure (9000 PSIG). In parallel, a gasometer was used to measure the GOR of an aliquot sampled from the high-pressure bottle. Finally, this sample was characterized in the high-pressure viscosimeter.

The high-pressure interfacial tension measurement was carried out using a gas mixture of CO<sub>2</sub> and

CH<sub>4</sub> (0,82 and 0,18 mole fraction respectively) with the dead oil. The pendant drop technique was used.

## Results and Discussion

### Characterization of the dead oil sample

Tab. (1) shows the measured properties of the dead oil sample used in this study. In Fig. (1) the density line is presented and the Tab. (2) shows the same data with some interpolations and extrapolation (\*).

Table 1: Density, water content and molar mass.

Property	Average	Standard deviation
°API <sup>(1)</sup>	35.533	0.00577
Density <sup>(1)</sup>	0.846	1E-05
Water content <sup>(2)</sup> (%vol)	0.006	0.000577
Molar mass <sup>(3)</sup> (g/gmol)	216.77	1.497

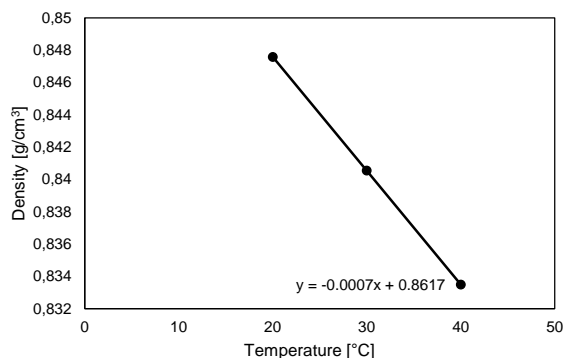


Figure 1: Density line.

Table 2: Oil density versus temperature.

T [°C]	$\rho$ [g/cm <sup>3</sup> ]
20	0.84758
21.5	0.84665*
30	0.84055
40	0.83349
41	0.833*
50	0.8267*
64.5	0.81655*

Table 3 and Figs. (2-3) show the results of crude oil viscosity at ambient pressure. The Arrhenius relation was used to approach a line in Fig. (3). It seems that there is an inclination change which could represent a transition like paraffin precipitation.

Table 3: Dead oil viscosity results.

Viscosities ( $\nu$ - kinematic e $\mu$ - dynamic)				
T [°C]	$\nu_1$ [mm <sup>2</sup> /s]	$\nu_2$ [mm <sup>2</sup> /s]	$\nu_{\text{mean}}$ [mm <sup>2</sup> /s]	$\mu_{\text{mean}}$ [cP]
21.5	8.781	8.936	8.858	7.500
30	6.091	6.053	6.072	5.104
41	4.633	4.720	4.677	3.896
50	3.894	3.898	3.896	3.221
64.5	3.012	2.995	3.003	2.452

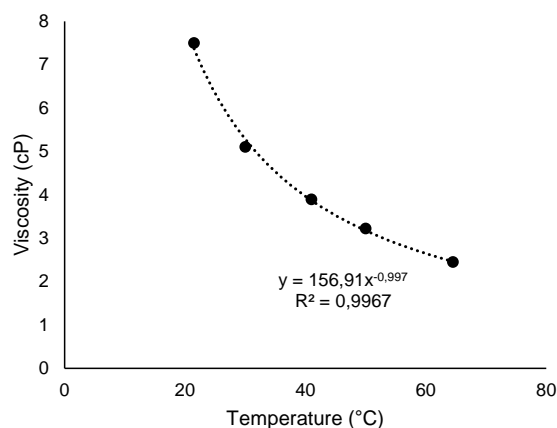


Figure 2: Viscosity versus temperature.

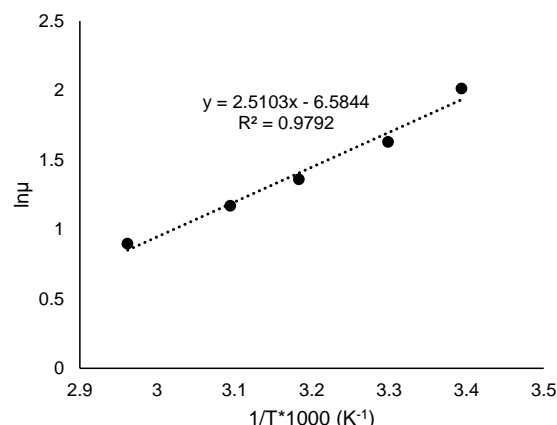


Figure 3: Viscosity versus temperature (Arrhenius plot).

### Fluid characterization

Table 4 shows the molar composition of the gas combined in the piston cell shown in Fig. (4) and maintained at 9000 PSIG. The order of addition for recombination was dead oil, CO<sub>2</sub> and CH<sub>4</sub>. NIST tables were used to obtain the density of CO<sub>2</sub> and CH<sub>4</sub> at pressure (5000 and 9000 PSIG, respectively) and temperature of injection (21.5 °C). It is worth to note that the resulting molar weight is almost the same as the CO<sub>2</sub> molar weight.

Table 4: Synthetic reservoir fluid composition.

Model fluid composition	
Zliq	0.03329
ZCO <sub>2</sub>	0.7917
ZCH <sub>4</sub>	0.1738
ZN <sub>2</sub>	0.00121
MM	44.882



Figure 4: The model fluid was combined in a floating piston bottle at 9000 PSIG.

The sample GOR was obtained by connecting a gasometer to measure the volume of gas at standard conditions, and measuring weight and density of the liquid resultant from the flash procedure. This result is shown in Tab. (5).

Table 5: GOR of the synthetic live sample.

	Average	Deviation
<b>GOR</b> (m <sup>3</sup> Std/m <sup>3</sup> Std)	3116	89 (2,8%)

Table 6 shows the compositional analysis of the gas resultant from the flash procedure. It is possible to note that some of the components from the dead oil sample are present in the gas current. This is an implication of the recombination procedure.

Table 6: Gas composition after the flash.

% Molar	Average	Standard deviation
CO <sub>2</sub>	81.502	0.462
O <sub>2</sub>	0.000	0.000
N <sub>2</sub>	0.370	0.372
C1	17.986	0.087
C2	0.000	0.000
C3	0.000	0.000
IC4	0.003	0.006
NC4	0.003	0.006
IC5	0.020	0.000
NC5	0.030	0.000
C6	0.037	0.006
C7	0.032	0.004
C8	0.022	0.007
C9	0.000	0.000
C10	0.000	0.000

In Figure 5, it is possible to visualize the sample at 9000 PSIG and 64° C inside the PVT cell. The color of the sample is between brown and orange. Table 7 reports the initial conditions of the PVT cell.

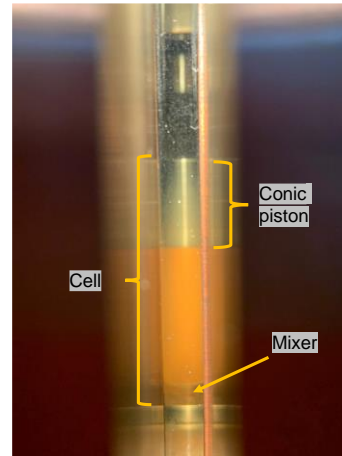


Figure 5: Fluid inside the PVT cell.

Table 7: PVT inicial setting.

<b>Initial pressure (PSIG)</b>	<b>9000</b>
<b>Temperature (°C)</b>	64.5
<b>Specific mass (g/cm<sup>3</sup>)</b>	0.82484
<b>Mass (g)</b>	19.498
<b>Initial volume (cm<sup>3</sup>)</b>	23.546
<b>Mol (mol)</b>	0.4327

### Constant composition expansion (CCE)

The sample was subjected to a controlled reduction of pressure from 9000 PSIG to around 1700 PSIG. The temperature of the experiment was 64,5 °C. The dew point was identified at 5900 psi. Above 5900 PSIG, the density was recorded, and below 5900 PSIG, the volume of liquid in the bottom of the cell was recorded, as well as the volume of the cell. The volume of the cell during the depressurization is shown in Fig. (6). It is possible to note that the compressibility of the gas phase increases around 3000 PSIG.

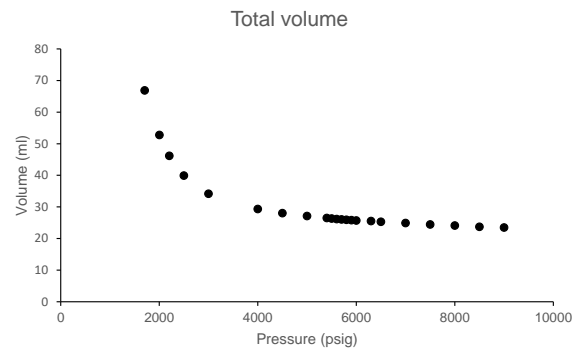


Figure 6: Total volume of the PVT cell during the experiment.

Figs. (7, 8, 9, 10 and 11) report the other CCE results. Figs. (7) shows the same data but in terms of volume ratio between the actual volume of the

cell and volume of the cell at saturation point. In Fig. (8), the compressibility factor of the undersaturated fluid is reported. The compressibility factor crosses the unity around 7000 PSIG. Fig. (9) indicates the volume of liquid condensed inside the cell during the expansion test. The percentage of liquid inside the cell is indicated in Fig. (10). Comparing Fig. (9) and Fig. (10), it is possible to conclude that the increase of the gas compressibility makes the liquid fraction to decrease even with the total volume of the liquid increasing. Fig. (11) indicates the liquid volume per volume of the cell at dew pressure.

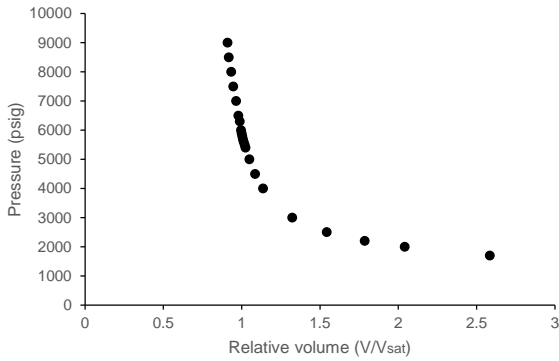


Figure 7: Relative volume in relation to the volume at dew point.

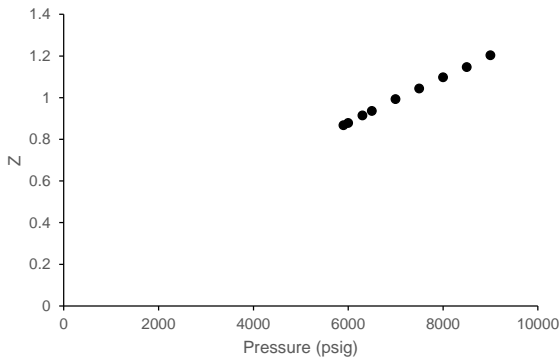


Figure 8: Gas compressibility factor.

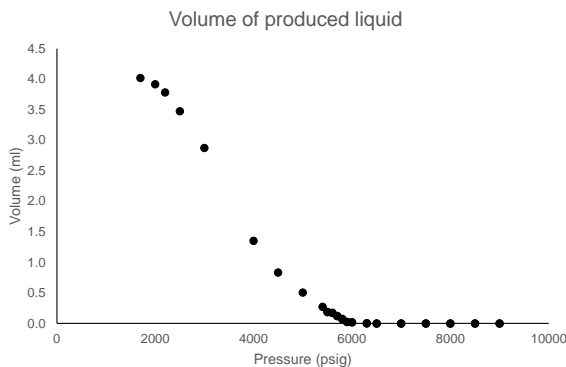


Figure 9: Volume of liquid inside the cell.

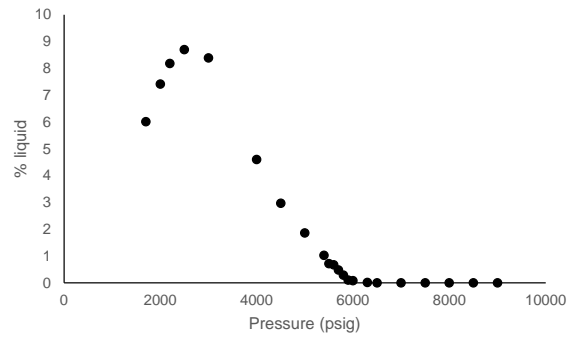


Figure 10: Fraction of liquid inside the cell.

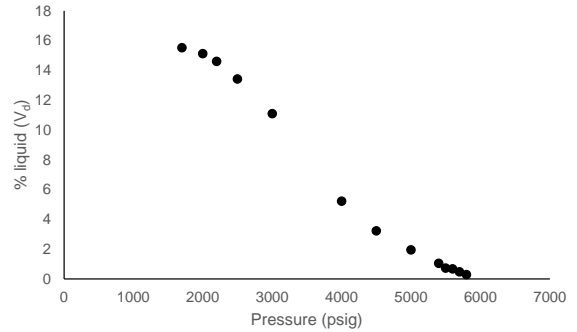


Figure 11: Liquid volume per volume of the cell at dew pressure.

### Constant volume depletion (CVD)

Fig. (12) shows a comparison of the volume of liquid inside the cell during the CEE and CVD procedures. CVD composition analysis was not possible due to low content of trackable compounds. For future studies, a possibility is to include propane in composition. As expected, the volume of the liquid of the CVD is less than the volume of liquid in the CCE at the end of experiments.

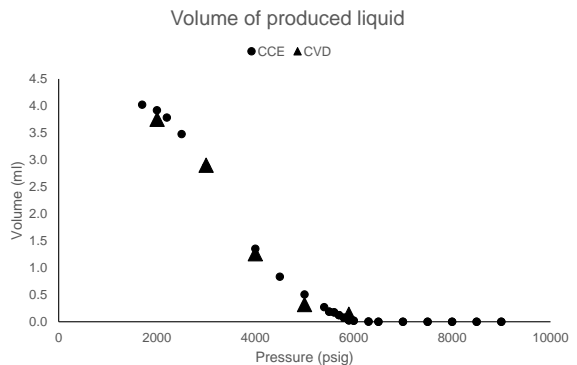


Figure 12: Comparison between CCE and CVD.

### High-pressure viscosity

Table 8 shows the high-pressure viscosities of the gas sample as a function of pressure. The viscosity was similar to the CO<sub>2</sub> viscosity at the same pressure and temperature, which is about one order of magnitude lower than reference water viscosity.

Table 8: High-pressure viscosity of the synthetic gas.

Pressure (PSIG)	Viscosity (cP)	Deviation	Temperature (°C)
9000	0.119	0.50%	64.2
8500	0.118	0.20%	64.3
8000	0.115	0.40%	64.5
7500	0.114	0.40%	64.5
7000	0.113	0.50%	64.5

### Interfacial tension

The exact gas content for the interfacial tension analysis is: CO<sub>2</sub> 81.726 %; CH<sub>4</sub> 18.149 %; N<sub>2</sub> 0.124 %. Table 9 and Figure 13 report the interfacial tension results at the temperature of 64.5 °C. It was not possible to measure interfacial tensions higher than the 1500 PSIG because the measuring drop cannot be formed.

According to Fig. (13), the fitting line crosses the x axis at 2388 PSIG. Therefore, the minimum miscibility pressure is 2388 PSIG according to the vanishing interfacial tension (VIT) method.

Table 9: Interfacial tension measurements.

Pressure (PSIG)	IFT average (mN/m)	Standard deviation
500	14.548	0.179
1000	10.695	0.239
1500	6.825	0.366

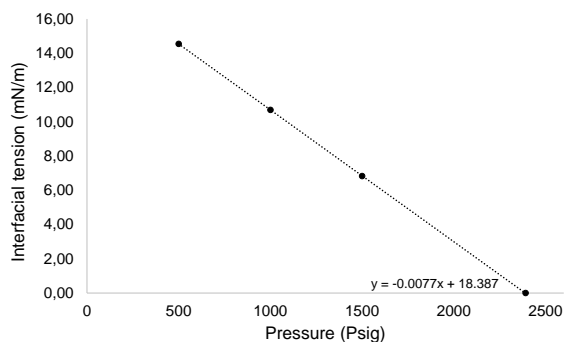


Figure 13: High-pressure interfacial tension.

## Discussion

The PVT behavior of a CO<sub>2</sub> rich mixture is analyzed in this paper. The class of fluid composition investigated herein is becoming more important since CO<sub>2</sub> dominant flows are expected to increasingly occur. Specifically, CO<sub>2</sub> is present in many Pre-salt reservoirs, and therefore CO<sub>2</sub> rich flows with hydrocarbons must be modeled using reliable volumetric data. In the present research, the phase behavior of a mixture containing dead oil, CO<sub>2</sub> and CH<sub>4</sub> is investigated and some aspects are addressed in this section.

According to the results, the density of the gas varied between 0.825 g/cm<sup>3</sup> at 9000 PSIG and 0.753 g/cm<sup>3</sup> at 6000 PSIG. Thus, the gas is dense.

Decreasing the pressure below the dew pressure (5900 PSIG), the lighter phase showed relatively low compressibility until more or less 3000 PSIG. As the gas become more compressible, the volume fraction of liquid decreases even with an increase in total liquid volume inside the cell. Fig. (13) shows a view of the phase behavior at 4300 PSIG. The condensed oil appears well separated from the lighter fluid phase.

This type of system containing high CO<sub>2</sub> content shows a substantial tendency of immiscibility. Also, a very small change in composition lead to a big change in the saturation pressure.

Therefore, high-pressures are needed for recombine the fluid. The pressure of 9000 PSIG was used for the recombination of the sample used in this work. The confirmation that the fluid recombined comprehends just one phase is the big difference between the recombination pressure (9000 PSIG) and the saturation pressure (5900 PSIG). When two phases are in the recombination cylinder, a saturated phase is sampled and the condensation readily takes place.

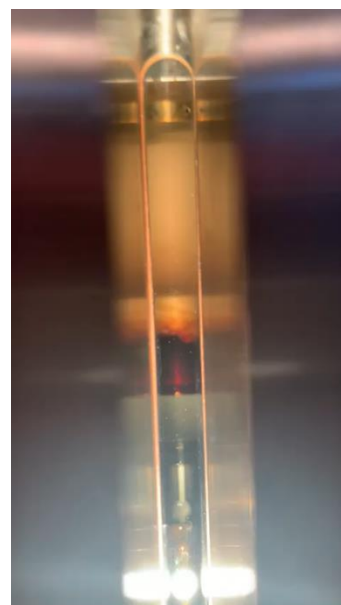


Figure 13: Phase behavior at 4300 PSIG.

Preliminary investigations show that it is possible to fit equation of state for this kind of fluid but when the temperature changes the fitting is no longer valid.

## Conclusion

In the present research, a synthetic reservoir fluid was prepared and analyzed in the laboratory. The workflow comprised low pressure essays with the dead oil, preliminary calculations, fluid recombination, PVT analysis, gas preparation for the interfacial tension measurements and finally interfacial tension measurements.

The procedure of calculation and recombination was successfully performed. The results indicated that major part of the liquid is condensed at the end

of the procedure (1700 PSIG). However, most part of the liquid (~70%) is already condensed when the pressure is about 3000 PSIG (below this pressure the fluid becomes more compressible).

The high-pressure viscosity of the undersaturated fluid was one order of magnitude below the water viscosity, and it is similar to CO<sub>2</sub> viscosity at the same condition.

Future investigations should include propane or butane in the global composition and studying other temperatures.

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## **Responsibility Notice**

The authors are the only responsible for the paper content.

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