



Phase behavior and fluid interactions of a CO₂-Light oil system at high pressures and temperatures



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ABSTRACT

This paper investigates the phase behavior and mutual interactions between a light crude oil and CO₂ at high pressures and high temperatures (HPHT). To do so, we have measured PVT properties of the CO₂-oil system at HPHT using a PVT setup. We have also tried to present a detailed methodology for measuring PVT properties of CO₂-oil systems and highlight the difficulties such as oil vaporization by CO₂ during the experiments. A crude oil sample, collected from a Malaysian oil field, was used here. Our experiments indicated that, CO₂ solubility in the oil increased at higher pressures when measured at a fixed temperature. Our experiments also showed that increasing the test temperature would reduce CO₂ solubility in the oil, while its effect is more significant at higher pressures. The swelling factor (SF) measurements showed an increasing trend with pressure up to a certain value so-called extraction pressure, at which, the SF started to be reduced even became less than one. The measurements of oil viscosity indicated that CO₂ dissolution in the oil sample could reduce the mixture viscosity up to 61%. The interfacial tensions between CO₂ and the crude oil at different pressures were also measured while the results were used to estimate the minimum miscibility pressure (MMP) and the first contact miscibility (FCM) pressure. The IFT measurements at various pressures displayed a reduction trend as a result of more CO₂ dissolution in the oil but with two different slopes. That is, at lower pressure values, the measured IFTs were sharply reduced with pressure, while the reduction rate of the IFT became less when pressures exceeded the extraction pressure. This study helps with determining the optimum pressure and temperature conditions of CO₂-oil systems to have a minimum IFT, a maximum CO₂ solubility and SF, and a minimum oil viscosity that are favorable for CO₂-enhanced oil recovery projects. Additionally, the methodology presented here gives guidelines on how to design PVT experiments of CO₂-oil systems for petroleum and chemical engineering applications.

1. Introduction

CO₂ injection has been considered as an efficient enhanced oil recovery (EOR) technique that has been under many studies recently [1, 2, 3, 4, 5, 6, 7]. During CO₂ flooding projects, CO₂ as a greenhouse gas can also be stored underground through various storage mechanisms, which has made it to be a favorable EOR-Storage method. However, for storage purpose, CO₂ is additionally and commonly being injected into saline aquifers [8, 9]. Different injection strategies can be applied during CO₂-EOR projects. These strategies include injecting CO₂ as a gas, e.g. continuous CO₂ injection and cyclic CO₂ injection (huff 'n' puff), or dissolved in water, e.g. carbonated water injection (CWI), and also alternating with water which is known as CO₂-WAG. The oil recovery process due to CO₂ injection is controlled by various mechanisms that mainly resulted from the high CO₂ solubility in oil. The displacement

process can be miscible or immiscible based on the reservoir conditions (pressure and temperature) and the composition of the oil [10, 11, 12, 13, 14, 15, 16, 17, 18].

It has been reported that the improvement in the oil recovery during CO₂ injection into reservoirs occurs mainly due to interaction between CO₂, oil and rock leading to favorable changes of oil and rock properties. These include: oil swelling, reduction in oil viscosity and CO₂-oil interfacial tension, extraction of light/intermediate oil components, and wettability alteration [19, 20]. The oil swelling due to the high CO₂ solubility in crude oils, is considered as one of the main oil recovery mechanisms in both miscible and immiscible CO₂ injections. The swollen oil has a higher saturation and therefore a higher relative permeability and mobility which directly affect the oil recovery. Oil swelling can also lead to the coalescence of disconnected oil blubs to become connected and make them a continuous phase with ability to be mobilized.

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Furthermore, the reduction in crude oil viscosity is also considered to be a favorable consequence of the high CO₂ solubility in crude oils. Although CO₂ was tested to be more effective in reducing heavy oil viscosity (can be as high as 98% [21]), it has a significant effect on improving the oil viscosity in light oil reservoirs especially at high pressures and relatively low temperatures. Previous studies reported that the interfacial tension of CO₂-oil systems is reduced during CO₂ injection in oil reservoirs. The reduction of the interfacial tension is more significant at high pressures [22, 23]. At high pressures, CO₂ can vaporize the light and intermediate components of the oil, which is considered as one of the oil recovery mechanisms, especially at high pressure reservoirs [24]. Fig. 1 highlights the main oil recovery mechanisms that can take place during CO₂ injection in oil reservoirs.

Many studies reported in the literature have investigated the mutual interactions between CO₂ and oils using various pressure-volume-temperature (PVT) experiments [25, 26]. The effect of CO₂ dissolution on oil swelling and oil viscosity reduction in gas-heavy oil systems was

investigated by Li et al. [27]. Their experimental results showed that the oil swelling and viscosity reduction were highly promoted by adding propane or n-butane to CO₂. Wei et al. [28] investigated the phase behavior of a CO₂-oil system. They measured the CO₂ solubility in oil and oil swelling factor, while they observed the extraction of the light and intermediate oil components by CO₂. Rudyk et al. [24] investigated the oil recovery by vaporization mechanism using supercritical CO₂ at various conditions of temperatures and pressures. Their results showed that crude oil vaporization by supercritical CO₂ can result in favorable recovery factors at high pressure reservoirs. Cao and Gu [29] studied the impact of operating temperature on the phase behavior of a CO₂-light oil system by carrying out some PVT tests. They measured the pressure at which CO₂ vaporizes oil (vaporization pressure), the onset pressure for asphaltene precipitation due to interaction of oil with CO₂, in addition to the minimum miscibility pressure (MMP). MMP was found to be more sensitive to the temperature as compared to the CO₂ vaporization pressure.

As it was previously discussed, the oil recovery mechanisms in any CO₂-EOR project are mainly related to the mutual interaction between phases in CO₂-oil systems. Therefore, it is highly important to investigate the behavior of CO₂ and oil phases at various reservoir conditions to have better understanding of the underlying mechanisms and better predict the reservoir performance. However, measuring the phase behavior of a CO₂-crude oil system in laboratory needs accurate and reliable methodology due to the challenges in measuring the CO₂ behavior when it is in contact with the oil, especially at high pressures and temperatures. Hence, the main objective of this paper is to comprehensively investigate the interactions between CO₂ and a light oil by studying their phase behaviors at all stages starting from CO₂ dissolution and oil swelling until achieving miscibility. Furthermore, an accurate and reliable PVT measurement procedure in laboratory is presented in detail, which is rarely found in the literature. In order to achieve this objective, a series of PVT experimental tests were conducted using a real light crude oil taken from a Malaysian oil field. First, PVT tests were conducted in a visual high pressure-high temperature (HPHT) PVT cell to measure CO₂ solubility and oil swelling. Second, the extraction of light and intermediate components of oil by CO₂ was quantified by measuring the compositions of the remaining oil phase in the PVT cell at high pressures. Third, the reduction in viscosity of the oil by CO₂ dissolution was measured at different pressures using an electromagnetic viscometer. Finally, axisymmetric drop shape analysis (ADSA) equipment was used at different pressures to measure the change of CO₂-oil IFTs and to obtain the MMP of our CO₂-light oil system.

2. Experimental

2.1. Materials

The crude oil sample was collected from one of the fields in Malaysia. It was a light dead oil sample having a density and viscosity equals to 812.9 kg/m³ and 2.21 mPa.s, respectively which were measured at atmospheric pressure and T = 25 °C. Fig. 2 shows the compositional analysis of the oil sample measured using a high-pressure gas chromatography. CO₂ gas with high purity (99.9%) was also used in this study. It is worth mentioning that the average reservoir temperature of the field is 95.5 °C, hence, all the measurements were carried out at this temperature, while some measurements were additionally re-conducted at 50 °C which approximately is the average temperature of the surface and the reservoir in the field.

2.2. Experimental apparatus

PVT setup. A Fluid Eval PVT system was used to study the CO₂-light oil interactions under various conditions. The main component of the PVT setup, shown in Fig. 3, is the PVT cell with having a sight glass for full viewing of the inside of the cell. It is also equipped with a magnetic

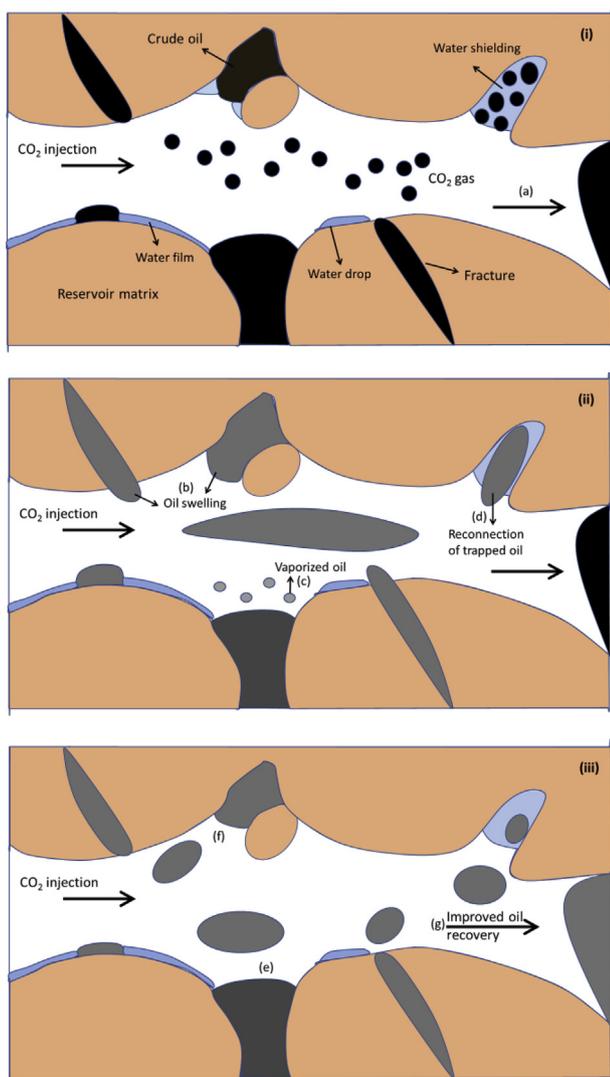


Fig. 1. Schematic of CO₂ injection in oil reservoirs. (a) oil produced by direct CO₂ displacement; (b) CO₂ dissolved in the crude oil caused oil swelling; (c) vaporized oil due to CO₂ extraction of light and intermediate oil components; (d) coalescing of disconnected oil ganglia by oil swelling; (e) The remaining components of crude oil after vaporization; (f) the residual oil in dead-end pores after displacing a part of swollen oil by CO₂; and (g) the improvement in oil recovery due to various CO₂ mechanisms. The dark color and the grey color represent the original oil and the oil after interaction with the injected CO₂, respectively.

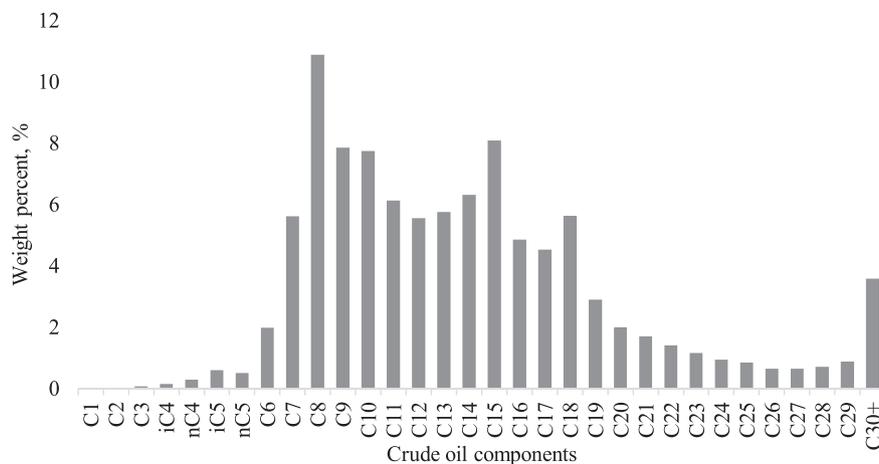


Fig. 2. Compositional analysis of the original crude oil sample.

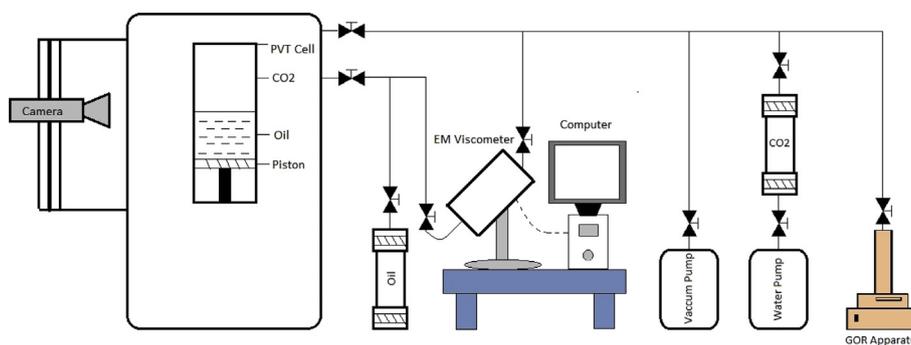


Fig. 3. Schematic diagram of the PVT setup.

stirrer. The pressure is controlled by a moving piston fitted internally into the cell. The system temperature is controlled by having the PVT cell been placed inside an oven where air bath controls the temperature. The gas-oil interface in the PVT cell can be captured through an integrated high-resolution camera. The data collected during the measurements, i.e. pressures, temperatures, volumes, and digital images are stored by an integrated computer data acquisition system. The volumes of the liberated gas at standard conditions are calculated by using a gas oil ratio (GOR) separator apparatus. Additionally, as shown in Fig. 3, an electromagnetic (EM) viscometer is connected to the PVT cell, hence the

viscosity of the oil-CO₂ mixture can also be measured. This PVT setup was used for measuring the solubility of CO₂ in the oil, oil swelling due to CO₂ dissolution, and viscosity of the CO₂-oil mixture. It should be noted that all the pressure and temperature gauges were calibrated before the tests. The accuracy of the pressure gauges, temperature gauges, and volume measurements are 0.1%, ±0.5°C, and 0.01 ml, respectively. Furthermore, some of the tests, e.g. the solubility test, were repeated to check the precision and reproducibility of the results.

ADSA setup. A schematic of the axisymmetric drop shape analysis (ADSA) setup used to measure the CO₂-oil interfacial tension is shown in

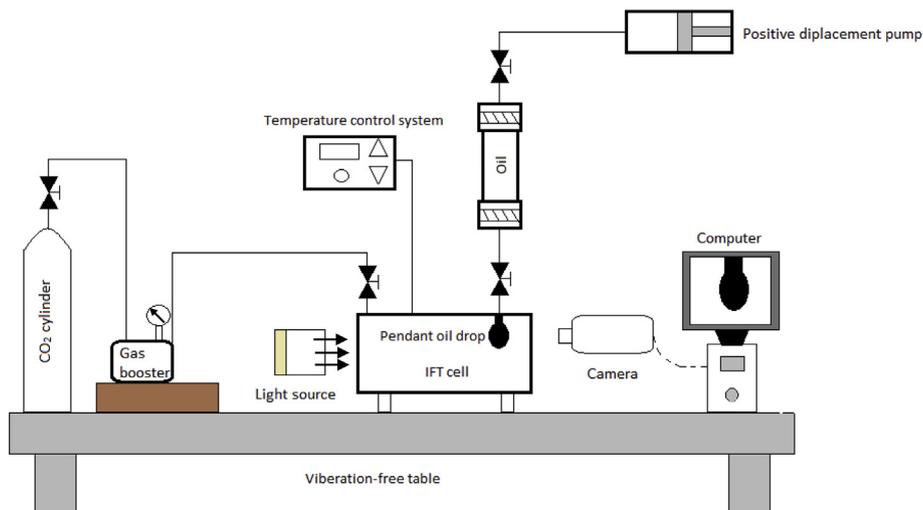


Fig. 4. Schematic diagram of the IFT measurement setup.

Fig. 4. The main component of the ADSA setup is the high-pressure windowed cell. A capillary needle positioned at the top of the high-pressure cell is used to create a pendant drop of fluid sample (oil here) inside the cell filled with fluid, e.g. CO₂. To introduce the CO₂ into the IFT cell, a gas booster is used to increase the pressure of the CO₂ gas above its cylinder pressure (6.2 MPa) in order to reach the required value (the pressure of the test). A high-resolution camera is used to capture the pendant oil drop images at uniform time intervals. The digital images are stored in a computer data acquisition system connected to the cell. The IFT cell is placed between a light source and the high-resolution camera on a vibration free table as shown in Fig. 4.

2.3. CO₂ solubility and oil swelling measurement

A common practice in the literature to measure CO₂ solubility in oils and the oil swelling, is to contact a certain amount of CO₂ with a certain amount (mass) of oil at HPHT conditions in a PVT cell, and the pressure of the system is recorded continuously. Later, the mass of dissolved CO₂ is calculated through the mass balance equation ($M_{CO_2, dissolved} = M_{CO_2, free}$ at initial state $- M_{CO_2, free}$ at final state) [30, 31]. In this practice, the volume of the free gas at initial and final conditions is determined visually through image analysis of the liquids in the cell. Hence, there is a high possibility of errors in CO₂ solubility and oil swelling measurements at various pressures. However, in this study, a more accurate and reliable procedure is used which is divided into two main steps; establishment of CO₂/oil equilibrium and isothermal depressurization. A schematic of the PVT setup that was used to measure the solubility and swelling, was shown before in Fig. 3.

2.3.1. Establishment of CO₂/oil equilibrium

This step includes preparation of the gas storage vessel, loading the oil sample into the PVT cell, and saturating oil with CO₂ in the cell. Before loading the CO₂ gas, the gas storage vessel was cleaned with acetone to remove any oil traces inside, then vacuumed for 30 min. Thereafter, the CO₂ gas was transferred to the vacuumed vessel, and the temperature was gradually increased to the desired value. The gas storage vessel was then pressurized to the required pressure using a water pump. After that, the PVT cell was tested for any leakage for 24 hours using nitrogen gas. Then, the cell was cleaned and vacuumed, and a specific volume of oil sample was transferred to the cell. The cell pressure and temperature were then increased to reach the experimental conditions (same conditions as the gas vessel). After the designed volume of CO₂ was injected into the PVT cell, the PVT cell was sealed and the magnetic stirrer was used. The cell was rocked for one hour to accelerate the dissolution process (by convective mass transfer) and quickly achieve equilibrium to ensure the oil is fully saturated with CO₂. It should be noted that the CO₂ was introduced into the cell step by step and at each step the cell was rocked, and the stirrer was used to accelerate the dissolution process. This procedure was followed to make sure that no excess CO₂ exists in the system at high pressures that can cause oil vaporization, and consequently errors in the measurements. After the oil was fully saturated with CO₂ in the cell, the system was left for 24 hours to be stabilized, while keeping the pressure of the PVT cell constant. This methodology can help to achieve rapid equilibrium between the CO₂ and the crude oil in the PVT cell.

2.3.2. Isothermal depressurization

The solubility of CO₂ in oil was measured by the method of isothermal depressurization. After the system has reached equilibrium, the volume of the CO₂-saturated oil was recorded at initial conditions. The pressure was reduced gradually step by step. At each step, the volume of oil saturated with CO₂ and the volume of liberated CO₂ gas were recorded. Additionally, the gas phase was removed manually at each step. The pressure was kept constant during expelling the free gas out of the cell. The free gas volume was determined at cell conditions by observing the change in the position of the piston. The released gas went through the GOR apparatus to also measure the volume of gas at standard conditions.

At each step, the cell pressure was decreased again to produce more CO₂ out of the mixture. This process was repeated several times until the atmospheric pressure was reached. Finally, the temperature of the cell was reduced to the standard value and the volume of residual oil was measured.

The swelling factor, SF, can be calculated using Eq. (1) [25].

$$SF = \frac{V_{o,final}(P_{test}, T_{test})}{V_{o,initial}(P_{atm}, T_{test})} \quad (1)$$

where $V_{o,final}$ is the volume of oil fully saturated with CO₂ at the test pressure and temperature, and $V_{o,initial}$ is the initial oil volume (free of CO₂) at atmospheric pressure and the test temperature.

2.4. Viscosity measurement

An electromagnetic viscometer (Vinci EV 1000) that was connected to the PVT setup, shown in Fig. 3, was used to measure the viscosity of oil saturated with CO₂. The viscosity measurements were carried out by analyzing the two-way travel time of a piston moving between two coils due to a magnetic field. The absolute viscosity of the mixture was measured automatically and recorded in the attached computer.

First, the electromagnetic viscometer was cleaned with acetone, vacuumed for 30 min, and heated to reach the required temperature. Then, the viscometer was connected to the PVT cell that holds an oil sample fully saturated with CO₂ at equilibrium conditions (see Fig. 3). In order to avoid any pressure drop and having phase separation and 2-phase flow system during transferring the sample to the viscometer, the viscometer and the connection lines were filled with CO₂ gas at a pressure equals to the condition of the PVT cell. The viscometer was set at vertical position to release the free CO₂ out until the CO₂-oil mixture was totally transferred. The reading of each oil viscosity measurement continued for 24 hours for each measuring pressure. This was because, the measurements showed fluctuation of readings before reaching a constant reading (after 3–4 hours), while we continued the readings for 24 hours to make sure that a stabilized reading is achieved. This step was repeated to measure the viscosity of oil fully saturated with CO₂ at 6 different pressures and at the constant temperature of 95.5 °C.

2.5. IFT measurement

The ADSA setup shown in Fig. 4, was used to measure the IFT of the CO₂-light oil system. First, the temperature of the IFT cell was increased to the designed test temperature ($T = 95.5$ °C). Then, the gas booster was used to inject the CO₂ gas to the cell at the required test pressure. The cell was left for pressure and temperature stabilization for 30 min before oil injection in to the cell. Thereafter, a pendant oil drop was created at the tip of the capillary needle by introducing the oil sample into the IFT cell. At each pressure step, the IFT measurements were repeated in average 4 times as at some trials a proper drop could not be formed at the tip of the needle. IFT values were recorded by the ADSA program once the camera detected a well-shaped oil drop. In this paper, we presented the IFT at various pressures and a constant temperature, $T = 95.5$ °C. The miscibility pressures, i.e., the CO₂-oil minimum miscibility pressure (MMP) and the first contact miscibility (FCM) pressure, were obtained from the measured IFT versus pressure data, using the vanishing interfacial tension (VIT) principal. This is based on the miscibility concept that occurs when the IFT between the two phases approaches zero.

3. Results and discussion

3.1. CO₂ solubility and oil swelling factor

CO₂ dissolution in crude oils is the key mechanism that leads to swelling of the oil, oil viscosity reduction, and interfacial tension reduction in any CO₂-EOR process. In this study, the CO₂ solubility was

measured at two different temperatures and various pressures as shown in Fig. 5. Regression analysis using a polynomial equation was employed to correlate the measured CO₂ solubility to the pressure, and the fitted equations are presented in the Table 1. The polynomial curves that fitted are also shown in Fig. 5. Fig. 5 clearly shows that the CO₂ solubility increases with pressure. This can be further explained that an increase in the pressure of gas will lead to the collision of CO₂ molecules with the CO₂-oil interface to be increased. Hence, more CO₂ is transferred and dissolved into the oil phase at higher pressures. On the other hand, Fig. 5 shows that increasing the temperature has a negative impact on the CO₂ solubility. The reduction in the solubility of CO₂ at higher temperatures is due to the increase in the kinetic energy of gas that overcomes the attractive forces between the gas and the crude oil molecules, and thereby reducing the CO₂ solubility. Moreover, Fig. 5 shows that the effect of temperature is more significant at higher pressures where there is a wider gap between the temperature curves at higher pressures. Additionally, the effect of CO₂ dissolution on changing the oil volume is shown in Fig. 6 obtained by monitoring oil volume in the cell. It is obvious that the swelling factor of the oil has increased with pressure as more CO₂ is dissolved in the oil at higher pressures. Furthermore, one can notice that the oil swelling factor curves are following the same trends as those of the CO₂ solubility plots indicating the direct relation between oil swelling and CO₂ solubility for a specific oil. It can be also noticed that directly after reaching the maximum swelling factor at a certain pressure of 8 MPa and 16.9 MPa at T = 50 °C and T = 95.5 °C, respectively, the trends of the oil swelling curves have steeply dropped as shown in Fig. 6. This is due to the high extraction ability of CO₂ to evaporate the light and intermediate components of the oil phase at these specific pressures, which is called here P_{high,ext}. It should be noted that these specific pressures are higher than the CO₂ critical pressure implying that the CO₂ has been at supercritical state considering the both temperatures tested are also above the critical temperature of CO₂. It is worth mentioning that, during running the tests, we have noticed that the vaporization of the oil components started even at lower pressures than those specific pressure values in Fig. 6. By expelling the gas out of the cell at different pressure steps and by observing the color of the CO₂ gas using the camera, minor oil vaporizations were noticed at pressures equal to 7.24 MPa and 15.58 MPa for T = 50 °C and T = 95.5 °C experiments, respectively named here as P_{minor,ext}. Most of the previous studied ignored the minor extraction pressure of CO₂ in PVT studies as the vaporization pressure was determined based on the image analysis to determine the volumes of the two phases in the PVT cell. The increase in the extraction pressure with temperature can be related to the CO₂ density at such conditions. CO₂ has a higher extraction ability at higher density values. As by increasing of the temperature, the density of CO₂ reduces, therefore, the extraction has happened at a higher pressure. As shown in Fig. 6, with further pressure increase, the CO₂ ability of extracting the light and intermediate components of the oil has increased, and consequently the oil shrinkage has been happened making the swelling factor curve to decline. Although the oil vaporization is

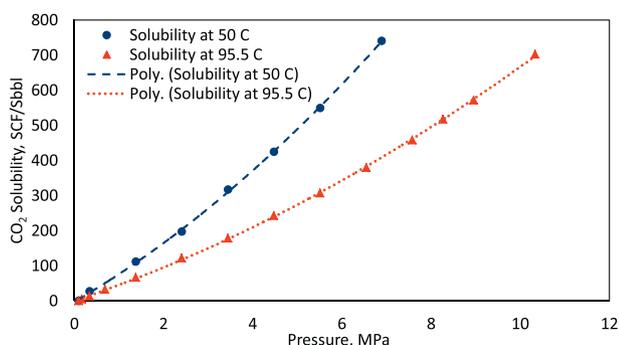


Fig. 5. The measured solubility of CO₂ in the light oil sample at various pressures and two different temperatures together with the polynomial curves fitted.

Table 1
Correlations of CO₂ solubility versus pressure at different temperatures.

CO ₂ solubility (Sol) (SCF/Sbbl)	Temperature (°C)
$Sol = 4.89 P^2 + 73.896 P - 3.1113$, $R^2 = 0.9997$	50
$Sol = 2.3779 P^2 + 42.869 P - 0.3664$, $R^2 = 0.9998$	95.5

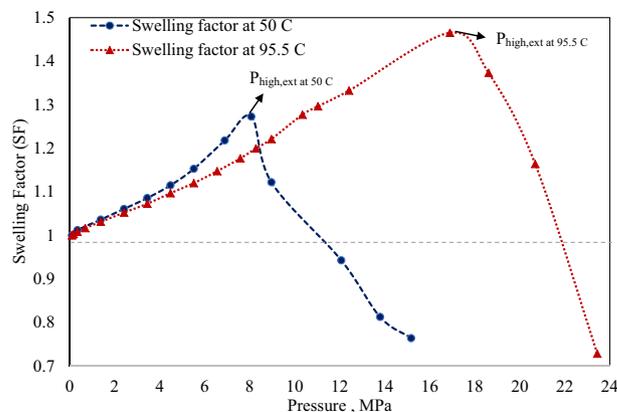


Fig. 6. The measured swelling factor of the oil in the CO₂-oil system at various pressures and two different temperatures.

dominant at pressures exceeding P_{high,ext}, oil swelling factor started to go below one, i.e. SF < 1, at higher pressures. This shows different stages of fluid interactions in a CO₂-oil system which should be considered particularly for achieving the miscibility as discussed later on.

3.2. Characterization of remaining oil

The compositional analysis of the original oil sample and the remaining oil in the PVT cell at the end of swelling test, i.e. at 23.4 MPa and T = 95.5 °C, are shown in Fig. 7. It is obvious from Fig. 7 that all the light oil components were removed from the remaining oil at this high pressure. Since the pressure at which the remaining oil was collected (23.4 MPa) exceeds the P_{high,ext}, the capability of CO₂ to extract the light and intermediate components from the original crude has been significant. Fig. 8 shows the composition of the original oil and the remaining oil when the components are lumped. One can notice that the light components C₂-C₅ were completely vaporized from the original oil sample at P = 23.4 MPa. Additionally, the mole percentage of the intermediate components C₆-C₁₂ was reduced from 60.1 % in the original oil sample to 34.9 % in the remaining oil. On the other side, the heavy oil components (C₁₃-C₁₉, C₂₀-C₂₉, and C₃₀₊) showed a relatively higher mole percentage in the remaining oil compared to the original oil sample. In other words, the higher quality part of the oil has come out with the

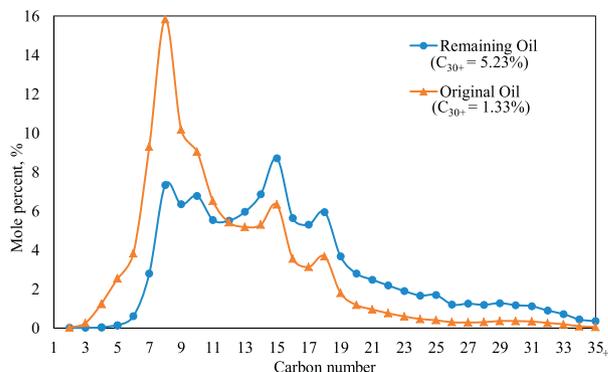


Fig. 7. Compositional analysis of the original oil sample and the remaining oil after the swelling test at P = 23.4 MPa and T = 95.5 °C.

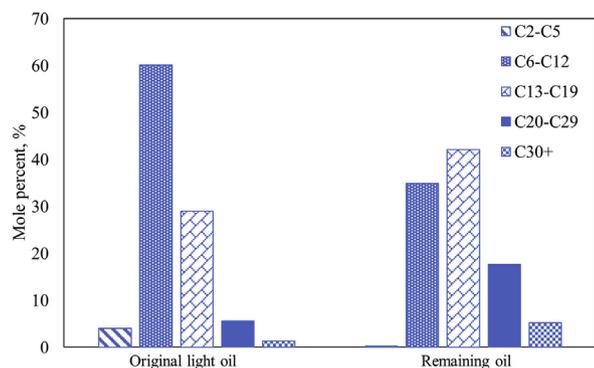


Fig. 8. Mole percent of grouped carbon numbers of the original light oil sample and the remaining oil after the swelling test at $P = 23.4$ MPa and $T = 95.5$ °C.

CO₂ gas at high pressures during expelling the gas out of the PVT cell. Therefore, the remaining oil in the PVT cell has different properties from the original oil sample. It was observed that, the heavy components of crude oil that remained in the cell at higher pressures had a higher viscosity compared to that of the original oil sample. This increase in the oil viscosity can cause unfavorable impacts on the volumetric sweep efficiency during CO₂ injection in oil reservoirs due to the reduction in the mobility of oil and the higher chances of viscous fingering. As a consequence, a relatively high residual oil saturations of the heavy oil components in the porous media may exist at high pressure injection scenarios needed for miscibility purpose. Hence, blowdown (depleting the reservoir pressure with a constant trend) at the end of CO₂ injection is recommended to utilize the benefit of CO₂ solution gas drive and reduce the residual heavy saturation [32]. It is worth mentioning here that at the end of the PVT test, the remaining oil at $P = 23.4$ MPa and $T = 95.5$ °C was collected by pressure depletion (blowdown) through a microvalve at the outlet when the remaining heavy oil part was coming out in the form of a fluid mixture having small bubbles of CO₂ gas. This produced mixture is known as foamy oil [33]. The foamy oil phenomenon has been proven to be an efficient production mechanism in the case of heavy oils in the experimental studies of CO₂-EOR, especially CO₂ huff 'n' puff process [33, 34].

Furthermore, it should be noted that the heavy oil components remaining in the porous media, after extraction of the light and intermediate components by CO₂, cause higher possibilities of asphaltene precipitation during miscible CO₂ flooding than during immiscible cases [35]. The asphaltene precipitation phenomenon in oil reservoirs has an adverse effect not only on the production of oil, but on the operational facilities as well. Therefore, the possibilities of formation of asphaltene perception should be well investigated before applying CO₂ flooding in oil reservoirs.

3.3. Oil viscosity reduction

The oil viscosity reduction as a consequence of CO₂ dissolution is one of the main mechanisms affecting the CO₂-EOR process. It is well known that, the reduction in the viscosity of oil directly affects the oil mobility and the fractional flow curve which leads to higher oil flow rates [36]. Previous experimental studies have shown that the oil viscosity reduction is dependent on the pressure, temperature and the amount of CO₂ dissolved in the oil [37]. The viscosity reduction effect by CO₂ dissolution is more significant in the case of heavy oils especially at low temperatures [26]. This is because of the high original viscosity of heavy oils especially at low temperatures which can be significantly reduced by CO₂ dissolution. Fig. 9 shows the viscosity of the oil sample saturated with CO₂ (mixture viscosity) at various pressures and the constant temperature of 95.5 °C. A polynomial equation was also fitted to relate the mixture viscosity to pressure as shown in Table 2. The polynomial curve that fitted is also indicated in Fig. 9. It can also be observed that CO₂

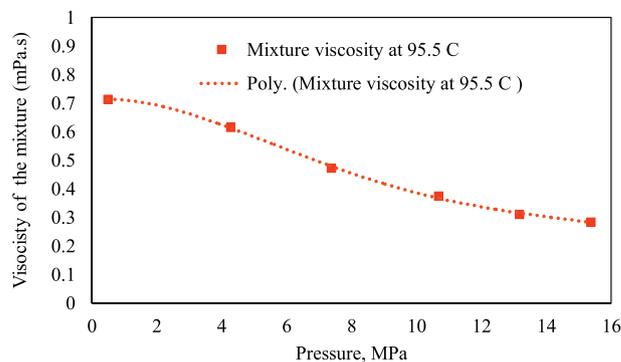


Fig. 9. Measured viscosity of oil saturated with CO₂ at various pressures and the constant temperature of 95.5 °C together with the polynomial curve fitted.

Table 2

Correlation of viscosity of oil saturated with CO₂ versus pressure at constant temperature.

Mixture viscosity (mPa.s)	Temperature (°C)
$\text{Mix. Vis.} = -2 \times 10^{-5} P^4 + 0.0009 P^3 - 0.0107 P^2 + 0.0078 P + 0.713, R^2 = 0.999$	

dissolution in the light oil sample has reduced the oil viscosity (oil free CO₂) from 0.72 mPa s at pressure near to the atmospheric pressure to 0.28 mPa s at 15.4 MPa (oil mixed with CO₂) which shows a 61 % reduction in the oil viscosity. It should be noted that that, the mixture viscosity measurements were terminated at pressure near to the extraction pressure, $P_{\text{minor,ext}}$ to avoid any change in the oil composition due to extraction of the light and intermediate oil components by CO₂ during saturating the oil sample in the PVT cell.

3.4. Equilibrium IFT and MMP

The equilibrium IFT was measured in this study for the CO₂-light oil system at 18 different pressures ranging from 0.4 MPa to 19.9 MPa, at $T = 95.5$ °C. It should be noted that, during measurements of IFT at a fixed pressure and temperature, IFT was changing by time (dynamic IFT) and took time to get a constant value, i.e., to get the equilibrium IFT value. Fig. 10 shows that the measured equilibrium IFTs decrease by increasing the pressure with two different linear trends; Trend A and Trend B. As depicted in Fig. 10, the equilibrium IFT is reduced from 20.3 mN/m at a low pressure until it reaches 1.9 mN/m at $P = 19.9$ MPa.

In Trend A, with pressure ranges from 0.4 MPa to 13.5 MPa, the governing mechanisms are CO₂ solubility in the oil with oil swelling. That is, by increasing the pressure up to 13.5 MPa, the CO₂ solubility has increased in the pendant oil drop formed at the tip of the needle that causes a significant reduction in the equilibrium IFT. While, by further increasing the pressure ($15.1 \text{ MPa} \leq P_{\text{eq}} \leq 19.9 \text{ MPa}$), the results show that the measured equilibrium interfacial tensions are decreasing linearly with a relatively lower slope. The slight reduction in the equilibrium IFT with pressure in Trend B is because of the extraction of oil components has been occurred by CO₂ in this region [31]. Hence, the measured equilibrium IFT in this pressure range (Trend B) is between an oil drop mainly formed of intermediate and heavy components and the surrounding CO₂ phase. A linear regression approach was applied to correlate the measured equilibrium IFT to pressure, as shown in Table 3.

The CO₂-oil minimum miscibility pressure (MMP) was also obtained from the measured equilibrium IFT data by using the vanishing interfacial tension (VIT) principal explaining that MMP corresponds to a zero IFT value. The MMP was obtained by extrapolating of the fitted line of Trend A as shown in Fig. 10. It should be noted that the miscibility pressure between the remaining intermediate and heavy components of

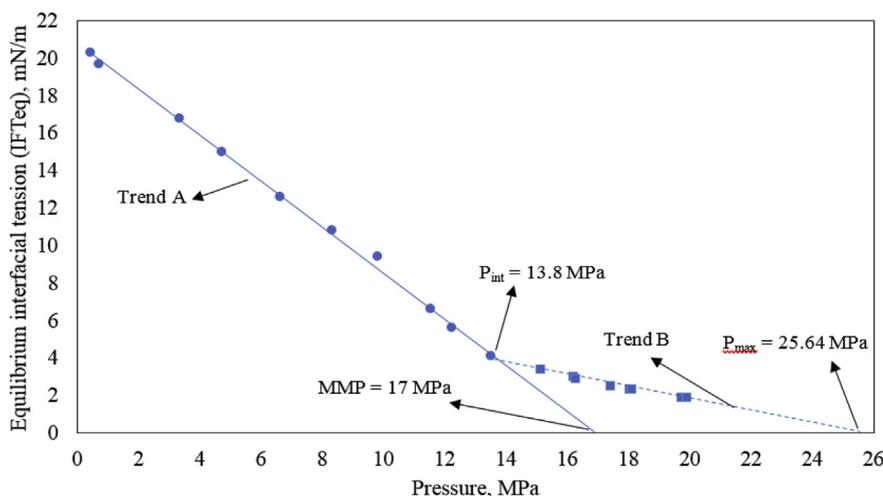


Fig. 10. Measured equilibrium interfacial tension between CO₂ and the light oil at various pressures and T = 95.5 °C.

Table 3

Correlations of equilibrium IFT versus pressure for two different pressure ranges.

	Equilibrium IFT (mN/m)	Pressure range (MPa)
Trend A	$IFT_{eq} = -1.2223 P + 20.768$ ($R^2 = 0.998$)	$(0.4 \leq P \leq 13.5)$
Trend B	$IFT_{eq} = -0.3132 P + 8.0319$ ($R^2 = 0.978$)	$(15.1 \leq P \leq 19.9)$

the oil and the surrounding CO₂ gas can be obtained from the extrapolation of the fitted line of Trend B. This pressure, known as P_{max}, is considered as the first contact miscibility (FCM) pressure [38]. The intersection pressure, P_{int}, between the two pressure regions (range A and range B) gives an estimate of the extraction pressure at which the light components of the crude oil start to be vaporized. Table 4 summarizes the important pressure points shown on Fig. 10.

In order to have a better understanding of the CO₂-light oil interactions, the pressure data obtained from the IFT measurements were also compared to the swelling test results conducted at the same temperature (T = 95.5 °C) presented before. It was found that the first observed extraction pressure, P_{minor,ext} = 15.58 MPa, during the solubility and swelling test, is slightly greater than the pressure range, 13.5 MPa ≤ P ≤ 15.1 MPa, at which the IFT trend has changed from Trend A to Trend B. Furthermore, one can notice from swelling test that the oil vaporization became significant at P_{high,ext} = 16.9 MPa which is consistent with the MMP = 17 MPa obtained from IFT experiment. The results of the IFT measurements suggest that oil recovery improvement during CO₂ injection in oil reservoirs is more likely to occur in the pressure range ‘A’ due to the high reduction of IFT in this pressure zone.

3.5. Oil recovery mechanisms at different stages

In this section the main oil recovery mechanisms that can take place during any CO₂-EOR process are summarized. As it was discussed earlier in this study, three main pressures; P_{minor,ext}, P_{high,ext} or MMP, and P_{max}, control the CO₂-oil interactions and phase behavior in a CO₂-light oil system. Table 5 defines the CO₂-EOR dominant recovery mechanisms in 4 pressure regions identified by the three onset pressures.

At pressures below P_{minor,ext}, the oil recovery is improved by the effect of oil swelling, viscosity reduction, and IFT reduction. Furthermore, it should be noted that CO₂ diffusion can improve the aforementioned recovery mechanisms especially at pore scale. By further increase in the pressure, i.e. P_{minor,ext} ≤ P ≤ P_{high,ext}/MMP, minor extraction of oil components is added to those key recovery mechanisms at the lower pressure range. By increasing the pressure beyond P_{high,ext} or MMP, the oil recovery is mainly controlled by the high capability of CO₂ to extract light/intermediate components of oil (vaporization gas drive, VGD,

Table 4

Important pressure points obtained from the equilibrium IFT measurements of the CO₂-light oil system at the fixed temperature of T = 95.5 °C.

P _{int} (MPa)	MMP (MPa)	P _{max} (FCM pressure) (MPa)
13.8	17	25.64

Table 5

Main oil recovery mechanisms that can occur at different pressures during CO₂-EOR processes.

P < P _{minor,ext}	P _{minor,ext} < P < P _{high,ext} /MMP	P _{high,ext} /MMP < P < P _{max} (FCM pressure)	P > P _{max} (FCM pressure)
Oil swelling + Viscosity reduction + IFT reduction	Oil swelling + Viscosity reduction + IFT reduction + Minor extraction of light oil components	High extraction of light/intermediate oil components (gradual miscibility development)	Miscibility

process) which leads to miscibility development. The miscibility between CO₂ and oil can take place immediately at pressures higher than P_{max}. Furthermore, based on the findings of this study, it is recommended to implement CO₂ injection at near miscible conditions (slightly lower than MMP) to achieve high reduction in IFT and oil viscosity, high SF and CO₂ solubility, and avoid the problems of asphaltene precipitations. Such results can provide a better insight into understanding the governing mechanisms affecting oil recovery at various pressures during CO₂ injection projects.

4. Conclusions

In this study, the phase behavior and the mutual interactions of a real light crude oil-CO₂ system were comprehensively investigated. A series of PVT tests, viscosity and IFT measurements were conducted at various conditions. The results showed that CO₂ could be more dissolved in the oil at higher pressures while oil vaporization due to CO₂ interaction with the oil was also observed at such high pressures. The effect of temperature on CO₂ dissolution process in the oil was found to be negative and was more significant at high pressures. That is, it was observed that at

low pressure values, CO₂ solubilities were just slightly higher when measured at a low temperature as compared to their corresponding values at a high temperature, while at high pressures they were significantly higher at the low temperature. Moreover, the reservoir temperature effect on vaporization and extractions of the oil light components was also clearly observed. It was found that at higher temperatures, oil vaporization by the injected CO₂ occurred at higher pressures. For instance, the extraction pressures, $P_{\text{high,ext}}$, at 95.5 °C and 50 °C were measured to be 16.9 MPa and 8 MPa, respectively. This shows a linear relation between the operating temperature and the CO₂ extraction pressure. Furthermore, the capability of CO₂ extraction at high pressures was proved by measuring the composition of the remaining oil in the PVT cell at $P = 23.4$ MPa (exceeding $P_{\text{high,ext}}$) and $T = 95.5$ °C. It was found that all the light components of the original oil and most of the intermediate components were extracted by the CO₂ at such conditions leaving the heavy oil components in the cell. Hence, asphaltene precipitation in light oil reservoirs under miscible CO₂ flooding should be considered. Additionally, CO₂ dissolution in the oil showed a high ability to reduce the crude oil viscosity even at high temperatures. That is, the oil viscosity reduction reached up to 61 % at $P = 15.4$ MPa and $T = 95.5$ °C. The results of the IFT measurements indicated that a significant improvement in oil recovery during CO₂ injection in light oil reservoirs is more likely to occur at pressure ranges lower than the MMP or the CO₂ extraction pressure, due to the high reduction in the IFT in this pressure region. Based on the findings of this study, it is recommended to implement CO₂ injection in light oil reservoirs at near miscible conditions to achieve high reduction in IFT and oil viscosity, high SF and CO₂ solubility, and avoid the problems of asphaltene precipitations. Such findings give some clues that can facilitate designing CO₂-EOR projects and help with identifying the governing recovery mechanisms at various reservoir conditions. This study also presented a comprehensive and practical experimental methodology to measure the fluid properties of CO₂-oil systems at HPHT conditions which has various applications in petroleum and chemical engineering fields.

Declarations

Author contribution statement

Jalal Foroozesh: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Mohamed Rezk: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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