

Experimental study of phase behavior: heavy oil mixed with hydrocarbon solvent

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Summary

The phase behavior of the heavy oil (12 wt.%) mixed with hydrocarbon solvent (88 wt.%) has been investigated experimentally via in-situ P-wave velocity and density measurement, density measurement of gas-exhausted oil, and phase behavior observation. Suspended asphaltenes are hardly identified by velocity and density measurement, but their deposition and solidification have been observed at a typical in-situ condition, 22°C and 5 MPa. Understanding their physical and chemical properties is important for studying the plugging formation caused by asphaltene in reservoir, production, and operation process.

Introduction

Injecting hydrocarbon solvent is one important method to improve heavy oil production. And phase behavior, especially asphaltenes' behavior is a key parameter in injection process. Asphaltene is generally insoluble in normal alkanes, such as propane, n-heptane and n-pentane; but it is soluble in some aromatic solvents, such as toluene, benzene and pyridine (Mullins et al., 2007). With the injection of hydrocarbon solvent (e.g., propane, n-heptane, hexane, n-pentane, etc.), variations of in-situ temperature, pressure and oil composition cause different behaviors of asphaltenes, such as reducing relative permeability, altering wettability, and with additional pressure dropping to block the flow in wellbore tubing, upstream process facilities and surface pipelines (Hirschberg et al., 1984; Kord et al., 2012; Shirani et al., 2012). Better understanding asphaltenes' behavior is basically crucial for the solvent-based injecting operation.

We have investigated physical properties of several solvent-based mixtures including the velocity and density of heavy oil mixed with toluene (Han and Sun, 2016), and the velocity and density of heavy oil mixed with hydrocarbon solvent (propane, n-heptane, hexane, n-pentane, etc.) (Han and Sun, 2017, 2015). In this research we focused on the phase behavior of heavy oil (12 wt.%) mixed with the high percentage of hydrocarbon solvent (12 wt.%).

2. Experimental methodology

To investigate phase behavior of heavy oil with hydrocarbon solvent at a typical in-situ condition of about 22°C and 5 MPa, the combined measurement system was used to measure ultrasonic P-wave velocity and density at the in-situ condition, to observe the phase behavior and bubble point pressure at the room temperature with decreasing pressure, and to observe asphaltenes' behavior simultaneously. Also we measured density of gas-exhausted oil.

2.1. Experimental apparatus and their calibrations

The measurement system is shown in Figure 1. The system consists of a sample storage vessel, a measuring vessel, and a visual PVT cell. The storage vessel stores the fluid sample and provides required pressure to the measuring vessel. The ultrasonic P-wave velocity of fluid sample is measured by a pair of transducers equipped on the both sides of the measuring vessel. It also measures the density of fluid sample via sample's volume and weight. Typically, we mainly use it to study physical properties of fluid at its single phase.

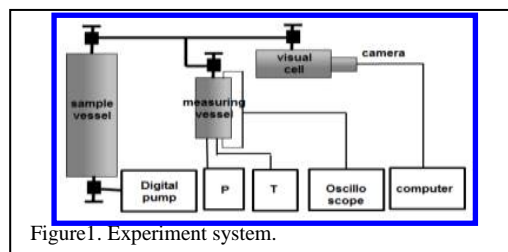


Figure 1. Experiment system.

For investigating phase behavior of fluid, a PVT cell works as shown in Figure 2. The two transparency buffers (glass) equipped on both sides allow us to observe fluid behavior. The webcam (Microsoft LifeCam Cinema 720p HD), equipped on the view side, allows us to observe and record fluid behavior directly, such as phase change, and bubble point present.

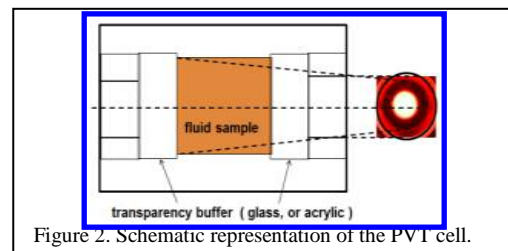


Figure 2. Schematic representation of the PVT cell.

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Measuring vessel calibration

Accuracy and correction of laboratory measurement is based on calibration of the measurement system. Because several factors, such as property of materials of the vessel components, inside shape of the vessel and O-ring, are affected by temperature and pressure, the volume and the distance between the acoustic transducers vary slightly with variation of temperature and pressure. Therefore, the measuring vessel was carefully calibrated as a function of pressure and temperature conditions. Vacuumed-distilled water was used as a standard sample. FLAG/Pbrine program was applied as a calibration standard for density and velocity of vacuumed-distilled water. Figure 3 shows the calibrated results. The red lines are the result of the standard calculation as mentioned above. The blue lines are measured result of the vacuumed-distilled water by the calibrated system, which has accuracy of density measurement of 0.9% and velocity measurement of 1.1%.

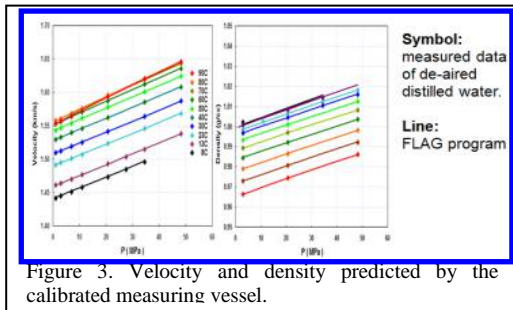


Figure 3. Velocity and density predicted by the calibrated measuring vessel.

PVT cell calibration for bubble point measurement

The PVT cell was calibrated for pressure measurement of bubble point at room temperature. The bubble point pressures of propane were used as a standard, which were obtained from NIST program. In Figure 4, red symbols are NIST data, and green symbols are measured by the calibrated PVT cell when a first bubble was observed from its window. The differences of observed bubble pressures with the NIST data are within 3 psia.

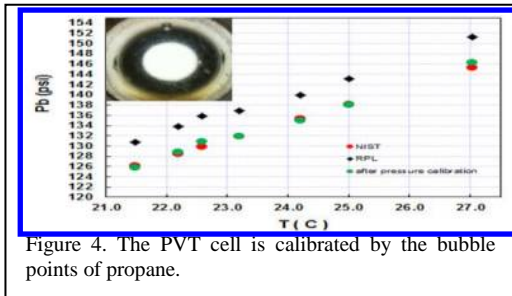


Figure 4. The PVT cell is calibrated by the bubble points of propane.

2.2. Material

To investigate initial phase behavior of heavy oil with hydrocarbon solvent, we selected the sample of heavy oil (12 wt.%) mixed with hydrocarbon solvent (88 wt.%). The hydrocarbon solvent was composed by propane (88 wt.%) and diluent (12 wt.%, mainly n-heptane+hexane+n-pentane, etc.). The high percentage of hydrocarbon solvent mixed with the heavy oil can cause the phase change of the mixture. And asphaltene precipitation, flocculation, and deposition may occur during pressure decreasing.

2.3. Experimental procedure

At the beginning, the experimental system was set up as shown in Figure 1. If multiple phases existed in the mixture, their gravitational accumulation was achieved by standing the sample storage vessel vertically during entire experiment period at room temperature and 5MPa. The measuring vessel was also set up vertically, but velocity was measured vertically and horizontally for testing sample's heterogeneity. The PVT cell was setup horizontally for phase observation.

After two weeks, the following seven steps were performed repeatedly until the entire sample was measured.

1. Clean and then vacuum the chambers of the measuring vessel and the PVT cell for 20 minutes;
2. To make sure that the same mixture is measured and observed in the measuring vessel and the PVT cell, the valve of the PVT cell is closed to let the mixture go to the chamber of the measuring vessel first;
3. Transfer the mixture through the top valve of the storage vessel to the measuring vessel slowly, and maintain the pressure of the mixture at 5 MPa during the transferring process by providing extra pressure via the digital pump;
4. Close the valve of the measuring vessel, and then close the top valve of the storage vessel;
5. Measure velocity and density of mixture in the measuring vessel at room temperature and 5 MPa. The velocity is measured vertically and horizontally via changing the position of the measuring vessel;
6. After the measurement, the mixture is transferred from the measuring vessel to the PVT cell for phase and bubble point observation. The pressure of the mixture is kept at 5 MPa during the transferring process;
7. Drop off the pressure of the mixture in the PVT cell step by step to observe and record phase behavior, and at near

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- bubble point, the pressure is decreased by 5 psi each time, and give enough time interval for phase equilibrium;
- Open the measuring vessel and the PVT cell to exhaust gas (propane);
 - Measure the density of the gas-exhausted oil at room conditions;
 - After some time interval, repeat the steps from 1 to 9 until the end of the sample in the storage vessel.

3. Results and discussion

After five cycles of experimental process, the mixture could not be pumped from the storage vessel to the measuring vessel any more even giving pressure up to 2,000 psi. The data of the five separate parts were measured from the top to the bottom of the mixture, and their phase behaviors were observed and recorded.

- The bubble points were observed in three parts as shown in Figure 5. The bubble point pressure could not be measured for Part Three and Part Four because one glass buffer leaked during the transfer of the mixture to the PVT cell. The three bubble points observed reveal two facts. One is that the viscosities of the mixture are different in the three sections. We know that the bubble point pressure is related to viscosity of the fluid. Generally, higher viscosity fluid has lower bubble point pressure at an isotherm condition.

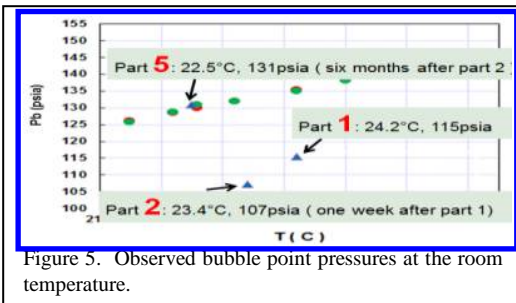


Figure 5. Observed bubble point pressures at the room temperature.

The bubble points indicate that viscosities of the mixture increase from Part One to Part Two, and then decrease to Part Five. We note that the bubble point pressure of Part Five is the highest one, and is almost the same as that of the pure propane, though it is the lowest part in the chamber of the storage vessel. One explanation is that the gravitational accumulation is a time consuming process. The lower bubble point of Part Two indicates that the heavier part is still suspended in the mixture after one week's interval

from Part One measurement. However, six months later, almost all of the heavier parts, mostly asphaltenes, are deposited in the chamber bottom of the storage vessel, and leave less viscosity in Part Five than in Part Two. The accumulation time also reveals that asphaltene as colloid may suspend in the mixture for longer enough to affect our measurement and monitory results.

- The measured densities of the gas-exhausted oil also support the above discussion (Figure 6). The accumulation and deposit of heavier particles are time dependent. At the short time, densities of the gas-exhausted oil increase from Part One to Part Three, and then decrease to Part Five after longer time.

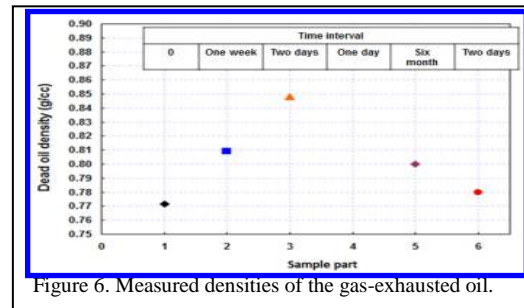


Figure 6. Measured densities of the gas-exhausted oil.

- That the dark particles can be observed in the picture of Part Two at 107 psia reveals that the heavier part is mainly asphaltene cluster, which does not appear in the observation of Part Five (Figure 7).

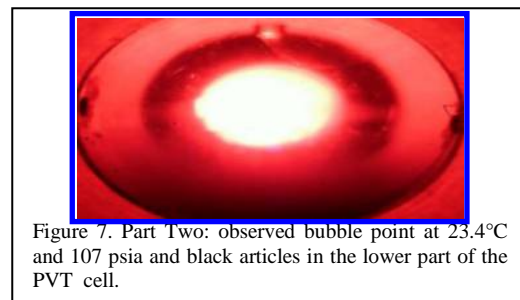


Figure 7. Part Two: observed bubble point at 23.4°C and 107 psia and black articles in the lower part of the PVT cell.

- Within the entire experiment period, the mixture in the storage vessel was kept at the room temperature and 5 MPa, and finally we collected asphaltenes deposited in the bottom part. Those reveal that asphaltene precipitation, flocculation, and deposition may occur during the long time period of gravitational accumulation in-situ conditions.

- The above phenomena are hardly identified from the measured data of P-wave velocity and density. As we

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mentioned before, suspended particles may be temporarily stable, and give the same velocity and density when we measure them from vertical and horizontal directions. There are no apparent differences among of the measured velocities and densities of the five parts. Because some part of heavy oil is dissolved in the solvent, the velocity and density of the mixture are higher than those of the solvent. On the other hand, the effect of the asphaltenes' behavior on the velocity and density of the mixture is ignorable at the measurement condition.

6. The measured velocity and density data also indicate that there are no multiple phases at the room temperature and 5 MPa, except for observed asphaltene behavior. If there are multiple phases, the light compound is mainly propane, which will go up to accumulate on the top of the mixture. But we still observed the bubble point caused by propane at Part Five of the mixture, and still observed propane gas exhausted from the last part.

7. At the pressure far above their bubble point pressure, we observed the process from equilibrium to un-equilibrium with pressure decreasing, and vice versa. (Figure 8).

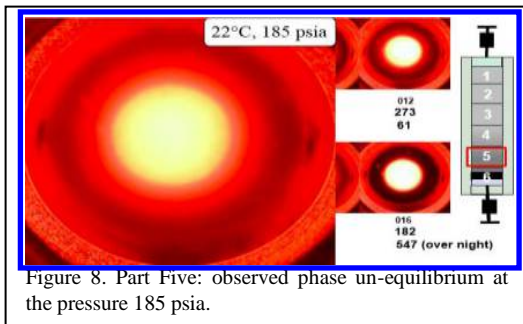


Figure 8. Part Five: observed phase un-equilibrium at the pressure 185 psia.

8. Solid asphaltene was collected from the storage vessel. Better understanding its physical and chemical process is crucial for us to reveal the same behavior happened in reservoir, production, and operation process.

At the last step, when the valve of mixture side was opened, nothing came out under 2,000 psi, because asphaltene sealed off the pipeline to the valve. But water was shooting out when the valve of the water side was opened, which was caused by exhausted propane gas from the mixture to push the piston within the storage vessel. That the propane gas is still in the last part of the mixture also indicates that it is not separated as a single light phase flowing to the top during the long time accumulation.

When the storage vessel was opened, we observed that the solid asphaltene was massively distributed in the whole chamber. Moreover, the shape of its distribution was alike suddenly frozen liquid (Figure 9). That means the solid phase of asphaltene or solid particle might occur or accumulate when propane was exhausting. To better understand the phenomena may give us a fundamentally important clue to understand the plugging formation caused by asphaltene. It can also help us to understand asphaltene properties from nano to macro scale at different operational conditions.

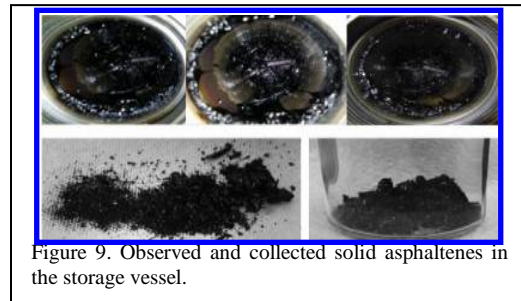


Figure 9. Observed and collected solid asphaltenes in the storage vessel.

4. Conclusions

Phase properties of heavy oil mixed with the hydrocarbon solvent were investigated via the four methods, in-situ velocity, density, gas-exhausted density, and phase behavior observation.

At a certain condition, asphaltenes are suspended stably in the mixture, and they may not be identified easily via velocity and density measurement.

The solidifying process of asphaltene has been observed, and to understand its physical and chemical process may help to understand the plugging formation caused by asphaltene in reservoir, production, and operation process.

The combined measurement system can be used to observe fluid phase behaviors, to measure bubble point, and dew point as a function of in-situ temperature and pressure.

Acknowledgements

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