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EXPERIMENTAL PHASE EQUILIBRIUM OF SULFUR HEXAFLUORIDE AND MINERAL OIL

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Abstract

Gas-liquid two-phase flow has substantial oil industry applications. The thermodynamic conditions related to the high pressures found in oil reservoirs approximate the mixture (oil and gas) to its critical pressure during the extraction. This approximation to the critical point makes it difficult to distinguish the two phases and approximates their densities effecting directly the flow patterns in pipelines. Such conditions are difficult to reproduce in laboratory scale, therefore a new mixture was proposed to emulate this two-phase density approximation using a high-density gas (SF_6) and a low-density liquid (mineral oil) working with lower pressures. In the present work, phase equilibrium data of mineral oil Hydra XP 32 and sulfur hexafluoride (SF_6) is determined at temperatures between 10 and 35ºC under different mixture mass concentrations (from 0.03 to 0.25 of SF_6) in order to evaluate its efficiency as a flow-model-mixture.

1. INTRODUCTION

Gas-liquid two-phase flow occurs in several industrial applications and the oil industry is one of them. Distinct models were and are still being developed along the last few decades in order to predict the flow patterns in pipelines, the pressure drop and the heat and mass transfer coefficients. However, these models were tested and validated to high-pressure flow, which is a typical application in the oil extraction in offshore production in just a few cases. The flow patterns cannot only vary depending on different geometrical conditions, but also on different thermodynamic conditions, which determine the phase behavior of the oil-gas mixture (Shoham, 2006). The IBP (*Instituto Brasileiro de Petroleo, Gas e Biocombustiveis*) points out that the concentration of CO_2 in Brazilian pre-salt reservoirs varying from 10 to 45% is higher than the accepted limits from ANP for commercialized gas, which is 3%. These high concentrations of carbon dioxide express a current great challenge in the oil extraction industry. The thermodynamic conditions related to the high pressures found in the reservoirs (higher than the CO_2 critical pressure) approximate the mixture to its critical pressure during the extraction. This approximation to the critical point makes it difficult to distinguish the two phases and approximates their densities effecting directly the flow patterns in pipelines. Such conditions are difficult to reproduce in laboratory scale, due to not only the great amount of energy, but also to the unsafe settings it needs. Therefore, a new mixture was proposed to emulate this two-phase density approximation using a high-density gas (SF_6) and a low-density liquid (mineral oil) in order to reproduce the conditions in lower pressure, and studying its thermodynamic behavior is key to understanding the flow patterns conditions.

In the present research, phase equilibrium data of mineral oil Hydra XP 32 and sulfur hexafluoride (SF_6) are determined at temperatures between 10 and 35ºC under different mixture mass concentrations (from 0.03 to 0.25 of SF_6). The isothermal synthetic method will be used and three different techniques will be compared (visual, ultrasonic

and pressure-volume observations) to determine mixture bubble points at different temperatures and point out different mixture behaviors. The main goal of this research is to identify if the binary mixture can be used as a model-fluid for simulating the critical high-pressure conditions found in the pre-salt reservoirs, and if so, determine the maximum pressure in which the two-phase system will be maintained under different system temperatures. The data produced by this research will be used on the project of a high-pressure flow loop in order to maintain the mixture in a two-phase flow avoiding three-phase state. It is important to mention that, phase equilibrium studies using SF_6 and vegetable oil were already taken by Ìlic et al. (2009) but none of them uses mineral oil, nor the synthetic method to evaluate the mixture thermodynamic behavior.

2. EXPERIMENTAL APPARATUS

Sulfur Hexafluoride (SF_6) was purchased from White Martins with purity of 99,9%. The mineral oil selected was the Lubrax Hydra XP 32 from PETROBRAS with specific gravity of 0,863.

Phase behavior is measured by using a high-pressure variable-volume cell. The cell is made of the stainless steel (AISI 316L) with internal volume up to 18 cm^3 and designed to operate in pressures up to 300 bar and temperatures up to 70°C. Figure 1 illustrates the equilibrium cell: project exploded view. The cell was projected to have flat lateral faces to connect the ultrasound transducers – Fig. 1(3) – and equipped with two sapphire windows – Fig.1 (2) and Fig. 1 (5) – for observing its content. The cell was built with three upper connections – Fig. 1 (4): two for temperature and pressure measurements and one for the gas feeding. Another connector – Fig. 1 (6) – was installed in the backside of the cell to control pneumatically the volume inside the cell.

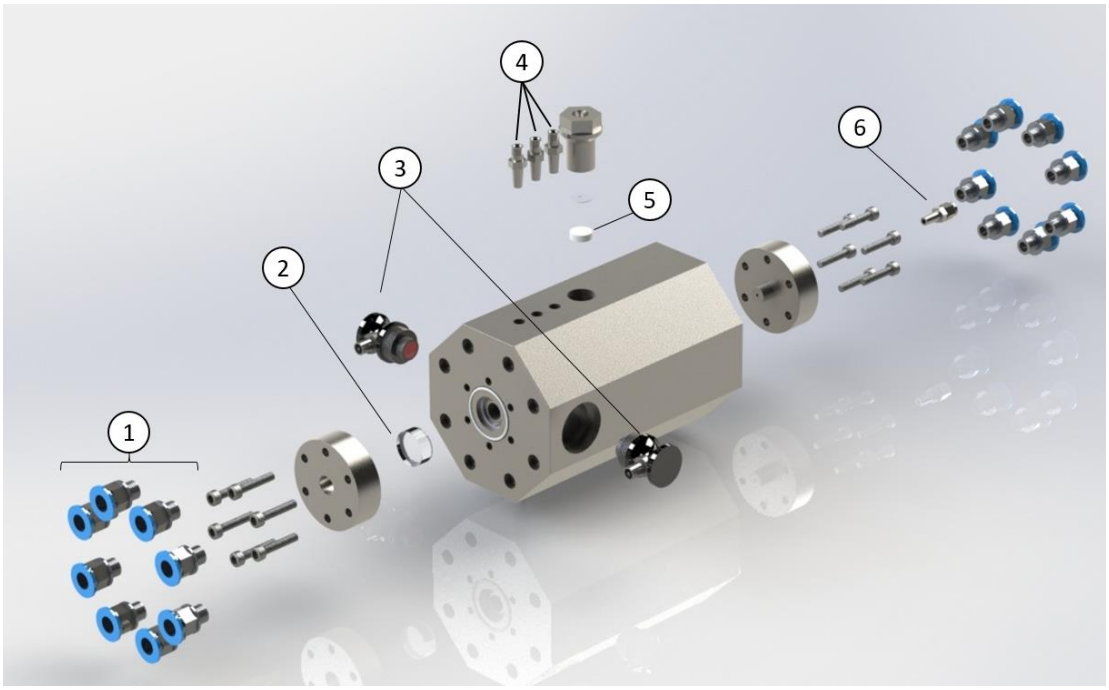

Figure 1. Exploded view of the project of the high-pressure variable volume cell.

The schematic drawing of the complete experimental apparatus for the phase equilibrium characterization is illustrated on Fig. 2. The system uses a syringe pump (Teledyne Isco 260HP) to feed the cell with SF_6. A stainless steel piston is used and connected pneumatically to another syringe pump (Teledyne Isco 260D) used to control the volume of the mixture inside the cell and the pressure during the experiment. This second pump is fed with an incompressible fluid making it possible to create a correlation between the volume inside the cell and the volume inside the pump. A magnetic stirrer (Gehaka AA-840) with stirring capacity of 22 liters of water is used to promote motion inside the cell for faster equilibrium achievement. A thermostatic bath (LAUDA Alpha RA 8) is used to control the temperature of the cell as well as the temperature of the SF_6-syringe pump. The bath fluid circulates on the walls of the equilibrium cell throw 16 connectors – Fig. 1 (1) – installed throughout the front and back face of the cell. For the ultrasonic measurements of the phase change, an acoustic signal is provided by a pulse generator and fed into the cell via a contact ultrasonic transducer (Olympus A603S-RB) of 1 MHz. A second, identical transducer monitors the signal at the other side of the cell. The resulting signal is amplified and displayed on a PXI computer. Temperatures were measured by using a RTD PT-100 (Omega P-M-1/10-1/8-6-0-P-3) intrusively and directly in contact with the mixture. Pressure measurements were carried out using a pressure transducer (Yokogawa EJX610A-C) connected to the interior of the

cell. One endoscope camera was used to enlighten and capture images of the mixture inside the cell. The actual complete experimental apparatus is shown on Figure. 3.

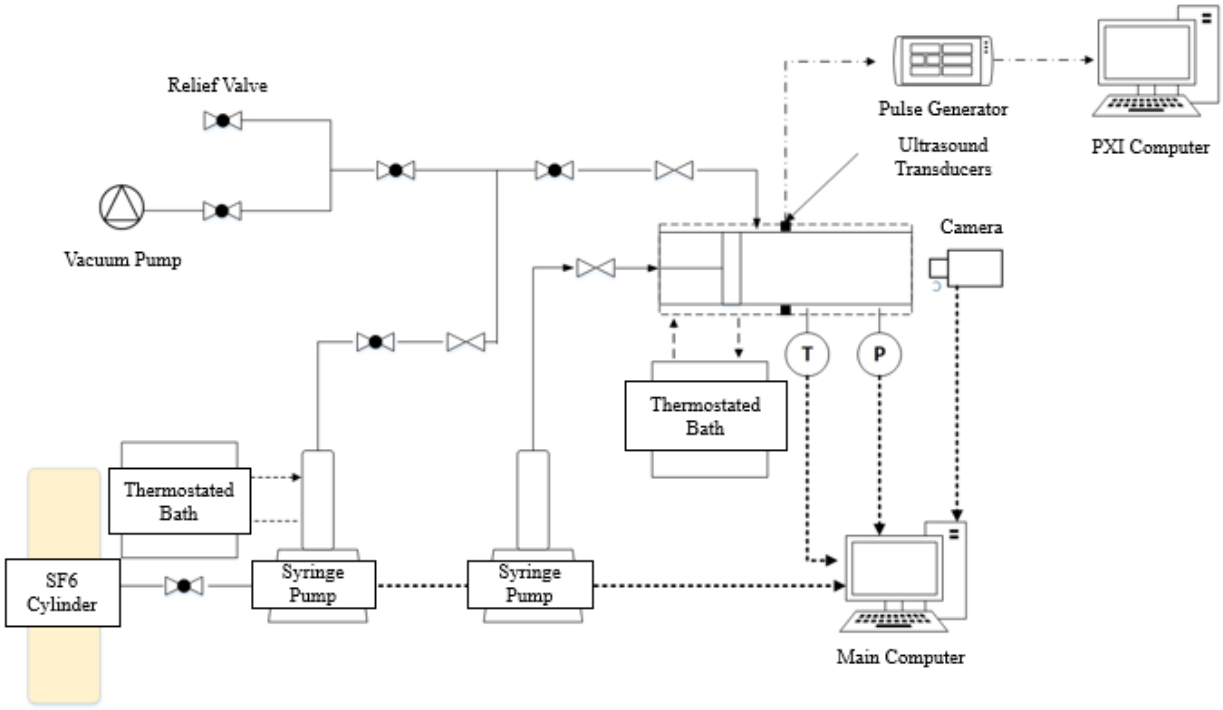

Figure 2. Schematic drawing of the experimental apparatus for the phase equilibrium characterization.

Figure 3. Photo of the actual complete experimental apparatus.

The validation of the experimental apparatus was carried out using pure fluid equilibrium measurements. Bubble points of pure SF_6 were evaluated for the temperatures varying from 5 to 25°C. Table 1 shows the results obtained using the two methods (visual by camera and P-V curves) and the error obtained for each technique at the pre-set temperature

compared with thermodynamic tables (EES – Engineering Equation Solver). It is possible to see that the P-V method resulted in smaller errors for the experiments.

Table 1. Bubble pressure experimental results and errors evaluated for the two different methods for SF_6 pure fluid for temperatures varying from 5 to 25°C. (N/M: Not measured).

Temperature (°C)	P_{bubble} (bar) (EES)	P_{bubble} (bar) (Camera)	Error (Camera)	P_{bubble} (bar) (P-V)	Error (P-V)	P_{bubble} (bar) (Ultrasound)	Error (Ultrasound)
5.0	14.56	14.90	2.35%	14.33	1.58%	N/M	N/M
10.0	16.52	16.40	0.69%	16.36	0.97%	16.75	1.41%
15.0	18.56	18.20	1.93%	18.40	0.86%	18.40	0.85%
20.0	20.75	20.31	2.11%	20.52	1.11%	20.56	0.89%
25.0	23.81	23.46	1.47%	23.60	0.88%	N/M	N/M

3. METHODOLOGY

The cell is first loaded with the predetermined amount of mineral oil and afterwards the SF_6 from a gas cylinder was cooled to a liquid state and compressed into the cell by a high-pressure syringe pump up to the desired pressure. The variation of volume inside the pump determinates the amount of SF_6 added to the mixture. The binary mixture is then heated and mixed with a magnetic stirrer until the operating temperature is reached. The system pressure is then increased until a monophasic liquid behavior is observed. The time to obtain the state of equilibrium varied from 1h to 24h. Bubble points were measured at constant temperature by increasing the volume of the cell and consecutively decreasing the system's pressure until the first bubble is observed. Visually, the phase equilibrium is noted when the first bubble can be visually detected by using the endoscope camera. It is important to mention that this technique is directly related to the quality of the pictures taken from inside the cell, as well as the experience of the person making the experiment, what could relate to errors of measuring. Figure 4 shows the appearance of the first bubble during a phase change process for the SF_6 pure fluid experiment used for the experimental apparatus validation mentioned before. The red circle marked on Fig. 4b indicates the bubble formation in the upper side of the cell; right next the PT-100.

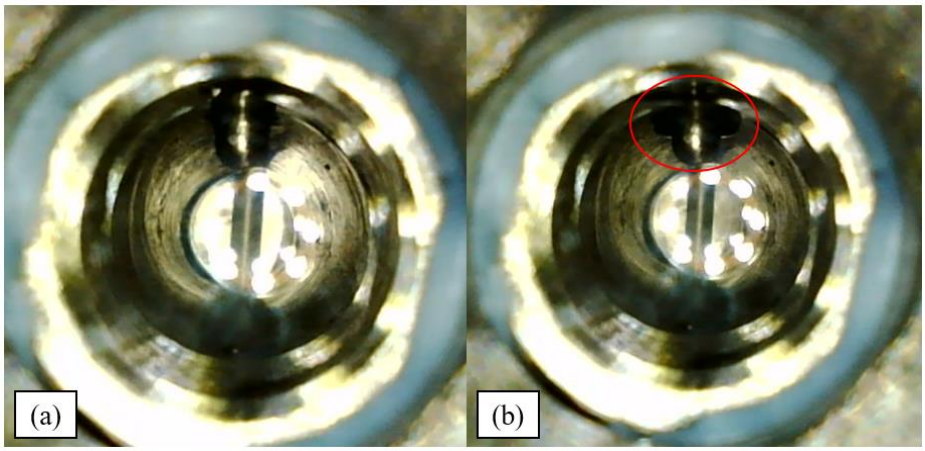

Figure 4. The bubble formation during the phase change of SF_6 pure fluid at 20°C and 20.31 bar.

By correlating the systems pressure with the volume inside the hydraulic syringe pump (pneumatically connected to the internal volume of the cell) it is possible to find a discontinuity behavior due to the phase change and it can also be used as a determinant of the bubble pressure as shown by Kato (2006). As mentioned before, the experiment starts with the mixture in its monophasic liquid form (Fig. 5a) and as the depressurization takes over (at constant temperature) the variation of the volume of the cell can be estimated evaluating the volume variation on the pneumatic pump. As the system is in its liquid (incompressible) state, small modifications in the volume of the cell leads to big variations in the pressure of the system. As the first bubble shows up (Fig 5b), a new compressible gaseous phase takes place leading to big change of the cell's volume even with small variations in the system pressure (Fig. 5c and 5d). The discontinuity of the pressure as function of cell volume can also be used as the determinant of the bubble pressure. Therefore, using

linear regression, it is possible to evaluate graphically the conditions of the phase change. Fig. 5 correlates the images taken during the phase change process to the graphical behavior for the P-V analysis for SF_6 pure fluid at 25°C.

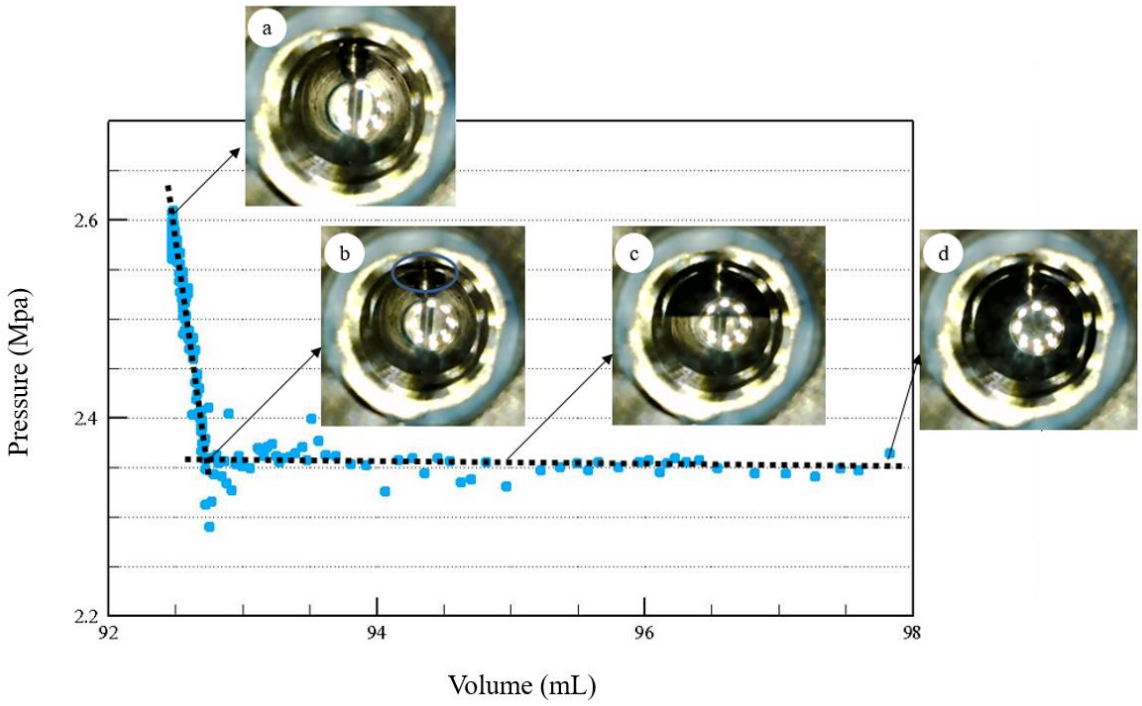

Figure 5. Graphical and visual behavior for the P-V analysis for SF_6 pure fluid at 25°C.

Ultrasonically, the drop on the medium energy from acoustic signal detects the phase change. Acoustic methods were already used for the determination of phase equilibrium data as shown by Kordikowski et al. (1998), but not evaluating the medium energy of the acoustic signal. Using acoustic measurements for phase equilibrium determination, a pair of transducers (one emitter and one receptor) have to be installed around the equilibrium cell on two parallel flat faces. They can be used to monitor sound speed and amplitude; and using an oscilloscope, it is possible to determinate the exact moment of the phase change. The main property analyzed during acoustic measurements using ultrasound is the isentropic compressibility (k_s) because of its direct relation with the speed of sound (u) as shown in Equation 1.

$$u = \sqrt{\frac{1}{k_s \rho}} \tag{1}$$

Using this definition, Daridon et al. (1998) were able to relate the variation on density (ρ) of a closed system due to the variation on its pressure (p), measuring the change on its speed of sound, as shown in Eq. 2; where p_0 is the initial pressure, T is the temperature, alpha is the coefficient of thermal expansion and C_p is the specific heat for constant pressure. Therefore, acoustic measurements under constant temperature can be used to verify the change in density due to the phase change and in fact, determine its exact time.

$$\rho(p,T) = \rho(p_0,T) + \int_{p_0}^{p} \frac{1}{u^2} dp + T \int_{p_0}^{p} \frac{\alpha^2}{C_p} dp \tag{2}$$

Cardozo (2011) used the acoustic technique and compared the results to the visual method. It was possible to note the variation in the signal obtained by the oscilloscope due to the apparition of a gaseous phase inside the cell as the signal's amplitude shrinks due to the loss of energy from the scattering of the ultrasonic wave inside the cell. The same behavior could be noticed during the experiments taken on the present work. Measuring the medium acoustic energy of the signals emitted over the time of experiment, the moment of the phase change can be determined with more clarity as it can be seen in Figure 6.

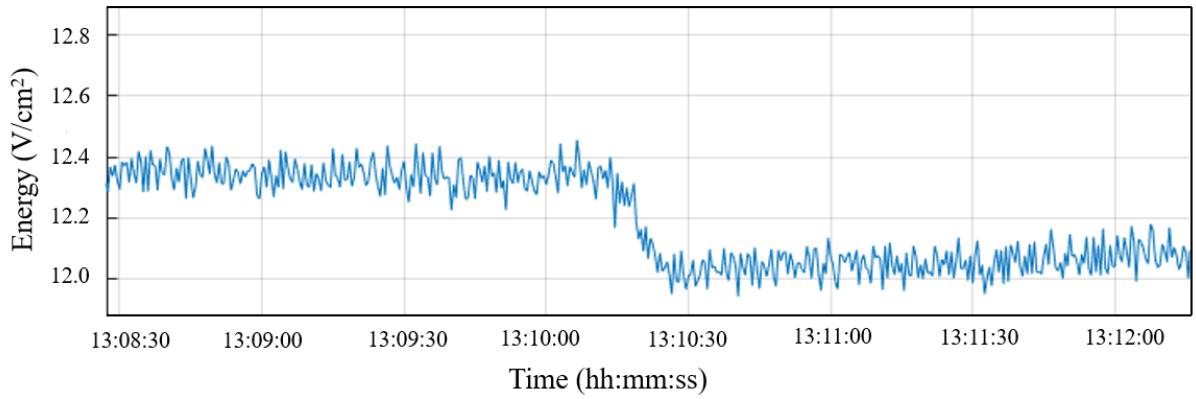

Figure 6. Acoustic medium energy signal drop behavior due during a gaseous phase formation for pure SF_6 at10°C.

4. RESULTS AND DISCUSSION

For the present work, phase equilibrium PVT data was taken for six mixtures with different global compositions of SF_6: 3.30, 5.20, 7.70, 10.96, 15.86 and 20.66 wt%. The system presented a large miscibility gap for the systems SF_6-mineral oil for all the temperatures measured (10, 15, 20, 25, 30 and 35°C). The experimental P-x data listed is shown in Figure 7. It is possible to see that increasing the temperature bubble pressure increases, but continues to be smaller than the vapor pressure of the pure SF_6. For the temperature of 35°C, it was also noticed that the miscibility gap starts do close, as a homogeneous mixture could be formed decreasing the bubble pressure significantly for the concentration of 5.20 wt%. It was not possible to obtain bubble points for concentrations lower than 3 wt% due to experimental apparatus' limitations.

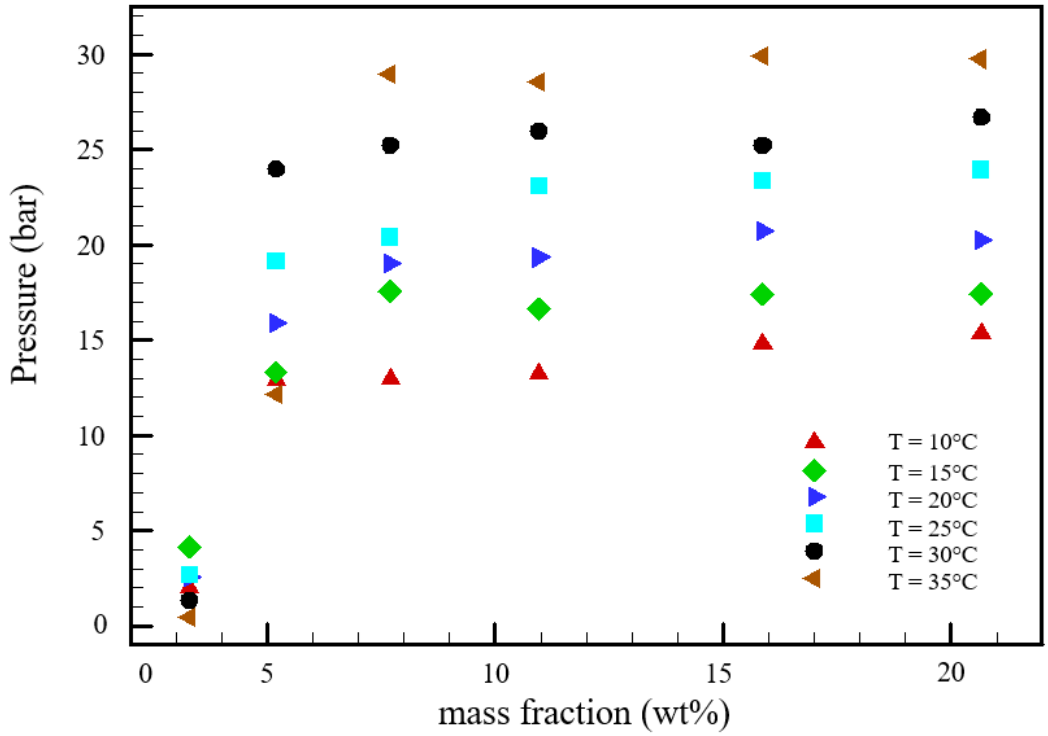

Figure 7. Bubble pressure for the system SF6-mineral oil for the temperatures 10, 15, 20, 25, 30 and 35°C.

Although the points acquired were majorly liquid-liquid-vapor equilibrium (LLVE) bubble points, some of them could be measured in the homogeneous region. All bubble points obtained for the lowest concentration measured (3.30 wt%) were liquid-vapor equilibrium (LVE bubble) with complete solubility of the SF_6 in mineral oil, as it can be checked by the pressure drop for the bubble points on Table 2. Another point in the diluted region was detected for the highest temperature measured (35°C) for the concentration of 5.20 wt% as it can be seen in Table 3. For those points,

the appearance of a small gaseous bubble could be detected on camera, but the slight variation of the systems volume was not enough to ensure the phase change. Fig. 7b shows the exact moment when the first bubble (circled in red) was visually detected at 1.35 bar, creating an LVE system for the concentration of 3.30 wt% of SF_6 at 30°C.

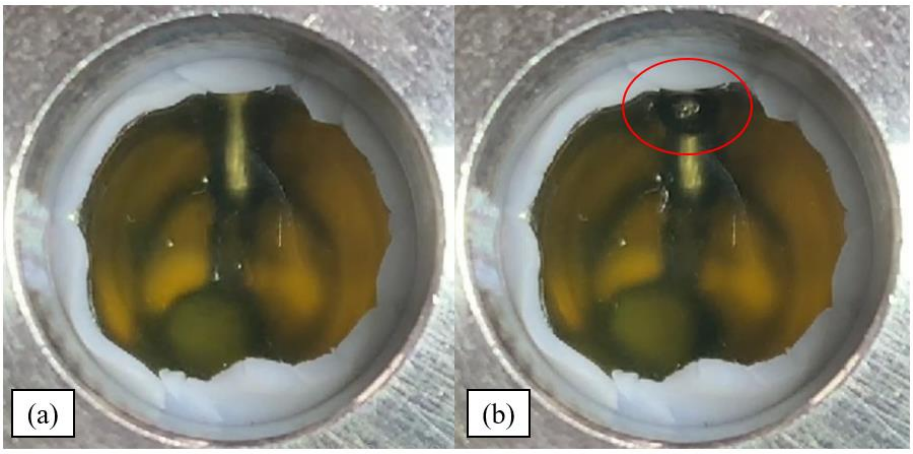

Figure 7. Visual detection of the phase transition for the system of 3.30 wt% of SF_6 at 30°C and 1.349 bar.

For the bubble points obtained out of the homogeneous region, the phase change was more abrupt than for the homogeneous one, rapidly increasing the mixture volume during the gaseous phase formation. Fig. 8 shows the volume behavior due to the pressure drop and gaseous phase formation for the system containing 15.87 wt% of SF_6 at 30°C.

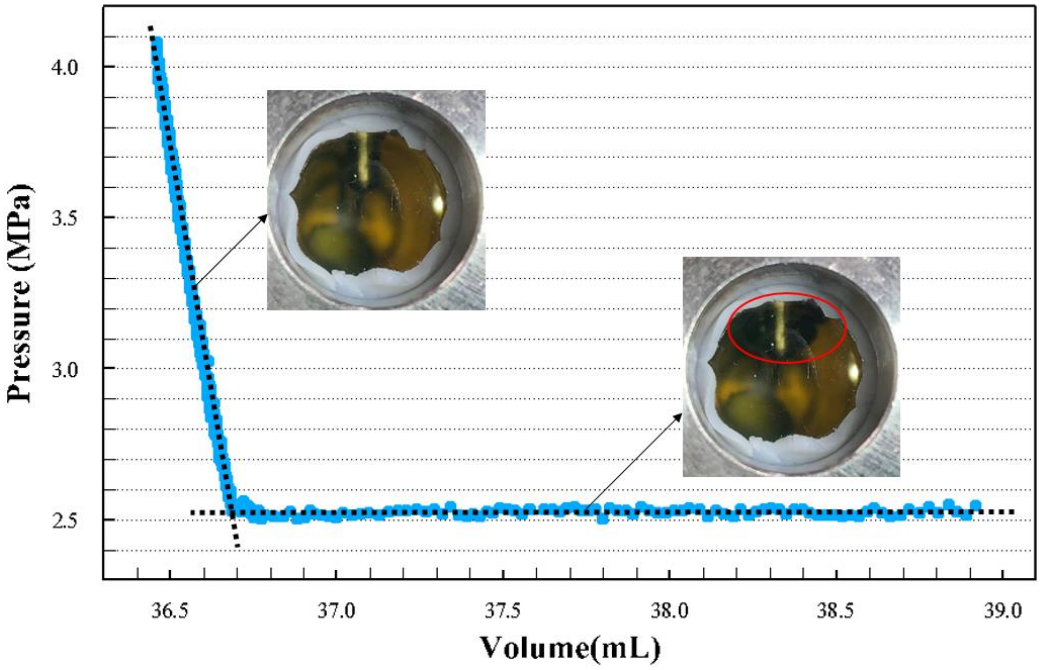

Figure 8. P-V behavior due during a gaseous phase formation for the system SF_6-mineral oil with 15.87 wt% of SF_6 at 30°C.

Differently from the other techniques, the ultrasonic method was able to measure the phase transition for all variety of temperatures and concentrations. This technique was able to detect the bubble formation when visually it was not possible. On the other hand, in some cases, the bubble formation was observed in areas out of range from the ultrasound transducer, taking more time to be acoustically noticed. Figure 9 shows the drop in the energy signal during the phase transition for the mixture containing 5.20 wt% of SF_6 at 35°C.

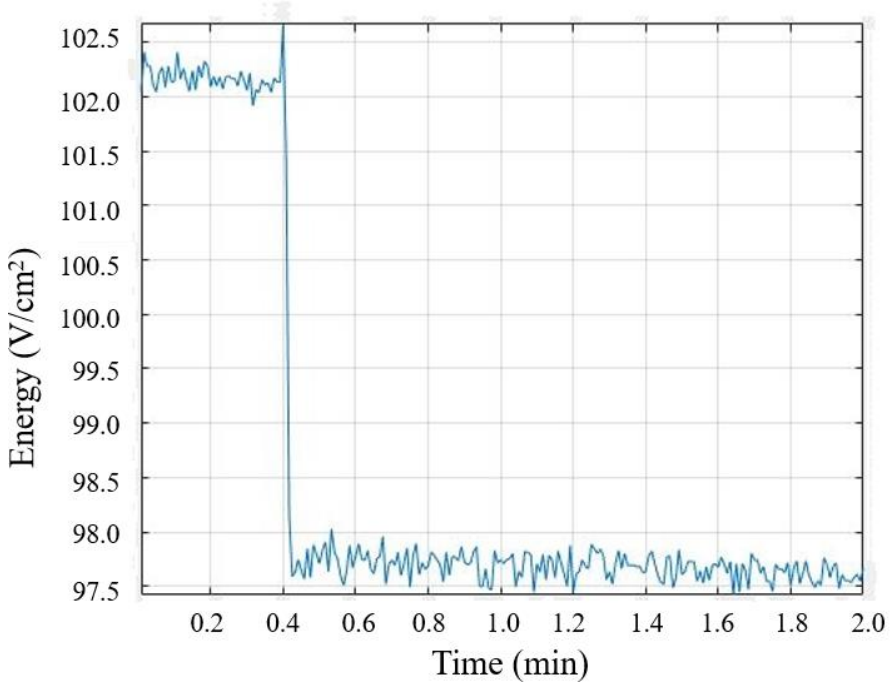

Figure 9. Acoustic medium energy signal drop behavior due during a gaseous phase formation for the system SF_6-mineral oil with 5.20 wt% of SF_6 at 35°C.

5. CONCLUSION

P-x data at 10, 15, 20, 25, 30 and 35°C for the system sulfur hexafluoride + mineral oil. The measured data show good agreement with the experimental gas solubility data available from literature. Three different techniques were used to identify the phase change, and it is important to note that some of the techniques used could not be able to verify the the bubble apparition for certain concentrations and temperatures. The main purpose of the present research is to obtain informations for the project of a high-pressure flow loop in order to maintain the mixture in a two-phase flow avoiding three-phase state. Therefore, to simulate in laboratory the critical conditions found during the extraction of oil in pre-salt reservoirs, it is important to maintain the system formed by SF_6 and mineral oil in pressures lower than the bubble pressures found in the present work for the temperatures of interest.

6. REFERENCES

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