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EXPERIMENTAL CHARACTERIZATION OF THE DEW POINT OF METHANE + ETHANOL MIXTURE

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Abstract. *The use of gas-lift lines for thermodynamics inhibitors injection to prevent hydrates formation may be a practical solution for wells already operating. However, as these lines are designed for gas only, the presence of liquids above certain quantities may damage some valves, indicating that these chemicals must be dissolved into the gas phase. Thus, it is important to know the phase envelope of the mixture of natural gas and thermodynamic inhibitor. Since methane is the main component of natural gas and one of the most used gas hydrate inhibitor is the ethanol, the system methane + ethanol is experimentally investigated in pressures up to 8.5 MPa and temperatures up to 353.15 K, with global composition above 93 % of methane, in order to determine the dew point of these mixtures. The synthetic isothermal experimental methodology is applied and two different techniques are utilized in order to properly determine the dew point: visual and acoustic. The experimental results will be compared against the commercial software for thermodynamic prediction Multiflash.*

Keywords: *dew-point, synthetic method, visual, ultrasonic, methane + ethanol*

1. INTRODUCTION

The gas-lift system is an artificial lift method applied in the offshore oil and gas production. This system relies on the energy of a compressed gas to aid the fluids reach the platform. This system is also used to deliver some chemicals (inhibitors and anti-agglomeration) into the production line, for hydrates prevention and management. This process, however, as showed by [(Daas et al., 2011), (Fleming et al, 2003) and (Poggesi, 2001)], may cause some reliability issues on the gas-lift system due to liquid precipitation inside the valves.

Since ethanol is one of the most popular hydrate inhibitor and methane is main gas found in the gas production, the present study was carried to provide some liquid-vapor equilibrium (ELV) of the binary system methane + ethanol, in order to predict the amount of inhibitor to be fed via gas-lift line without compromising the reliability of the system.

The phase equilibria of the methane + ethanol mixture has been studied by some authors [(Lannung and Gjaldbaek, 1960), (Boyer e Bircher, 1960), (Tokunaga et al., 1975), (Bo et al., 1993), (Ukai et al., 2002), (Friend et al., 2005), (Nourozieh et al., 2012), (Kapateh et al., 2015) and (Oliveira et al., 2015)], but very few have studied the dew point of this mixture [(Gupta et al., 1973), (Brunner and Hultenschmidt, 1989) and (Suzuki and Sue, 1990)]. Therefore, the objective of this work is provide the literature experimental data for the dew point of the methane + ethanol system at temperatures ranging from 313.15 K and 353.15 K and pressures up to 8.5 MPa. The experimental data generated in this study may be applicable to the oil and gas industry as well as optimizing thermodynamic models.

2. EXPERIMENTAL

2.1 Materials

The methane (99.995% purity) used in these experiments was supplied by White Martin, and the ethanol (99.9% purity) by Neon Comercial. Since the purity specifications were acceptable, no further purification method was applied to neither of components.

2.2 Apparatus

Figure 1 shows the schematic diagram of the pressure-volume-temperature (PVT) apparatus. This apparatus was used in other studies before (Miguel Jr, 2020). This apparatus consists of one equilibrium cell, which was designed in-house, two syringe pumps, one for gas dosage and one for liquid dosage and hydraulic pressurization of the cell, one camera, one thermal bath to control the temperature and the ultrasonic measurement system.

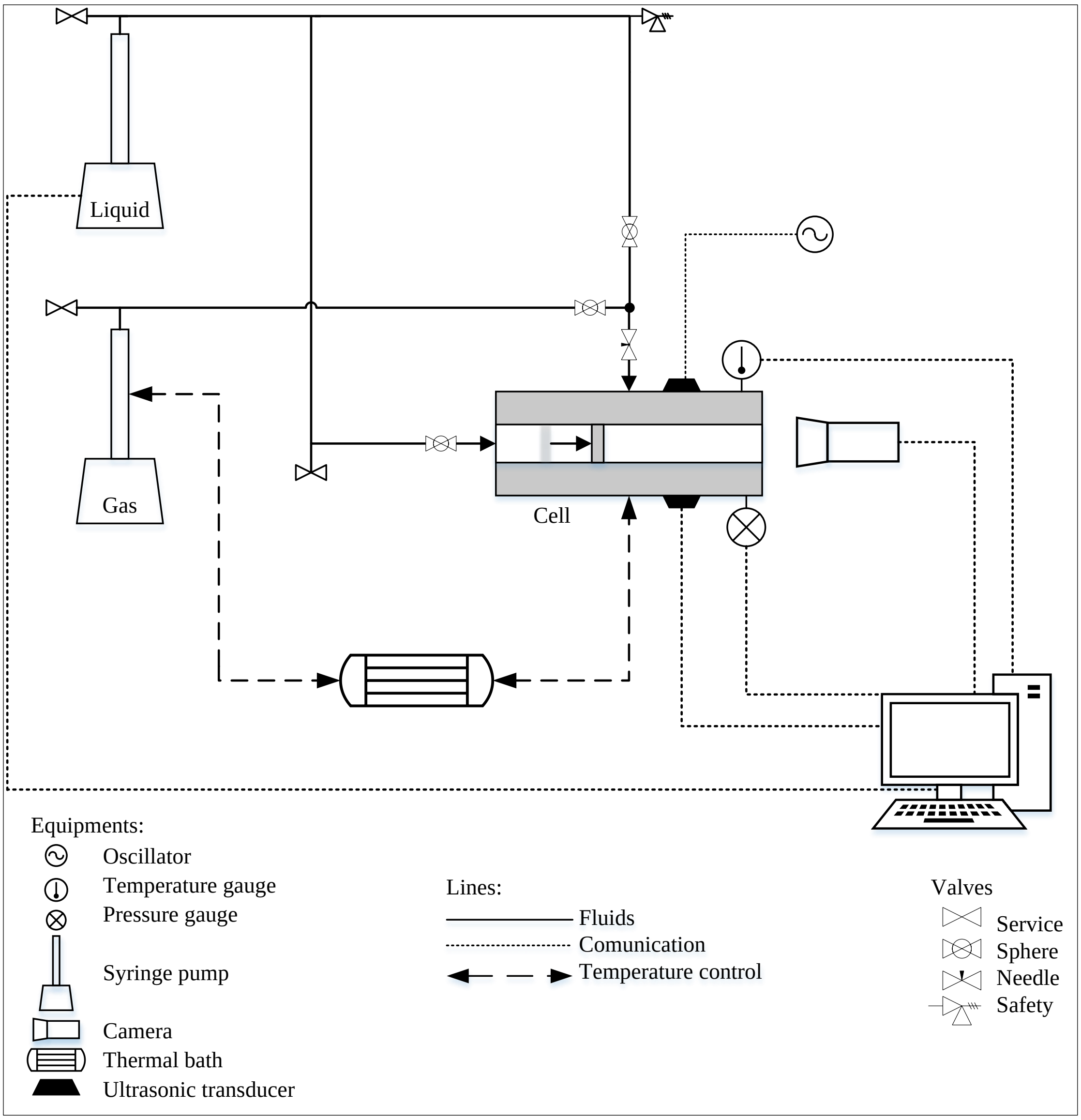
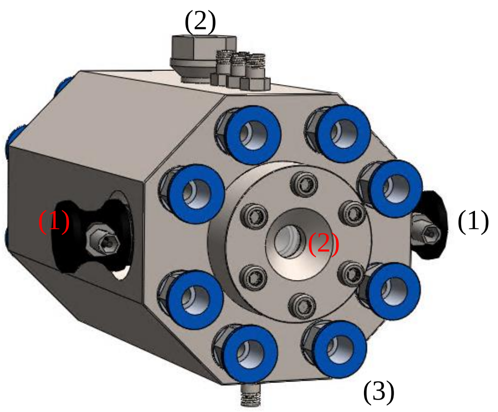


Figure 1. Schematic diagram of the experimental apparatus.

The equilibrium cell has a moveable piston, which allows increase the pressure inside the cell, two sapphire windows, one for illumination and the other one for recording, thermal circulation systems build-in to maintain the temperature constant within ± 0.15 K and it was designed to be coupled with ultrasonic transducers, for acoustic measurements. Therefore, the synthetic isothermal method was applied, and the visual and acoustic technique was used in order to detect the nucleation of the liquid phase inside the cell. Figure 2 shows the cell with ultrasonic transducers coupled, the position of the windows and the thermal bath circulation system.



(1) – Ultrassonic transducers
(2) – Saphire Windows
(3) – Thermal bath circulation system

Figure 2. Equilibrium cell.

The acoustic technique consists in measure the energy of an ultrasonic pulse between two transducers (emissor and receptor) through a fluid mixture. The signal is obtained by an oscillator and processed via a Matlab code.

2.3 Procedure

The experimental procedure was as follows: prior of each experimental the cell was evacuated. A precisely known amount of ethanol was inserted in the cell through the syringe pump. The remaining ethanol in the lines were removed with a vacuum pump. A precisely known amount of methane was inserted in the cell through the syringe pump. In order to control specific mass, the temperature was kept constant during the insertion and equal in the syringe pump and the cell, and the pressure in the syringe pump was the same before and after the insertion. The magnetic stirring and the temperate control was turned on. When the system reached the desired temperature, the pressurization steps (0.1 bar each minute), and the data acquisition started. The pressurization steps were made in the syringe pump supplied with liquid and it was hydraulic transmitted to the cell by means of the piston. After the system reached its dew point, the piston was pushed to the back of the cell, and a known amount of gas was inserted in the cell via syringe pump, changing the composition and the pressure of the system. After equilibration of the system, the pressurization and data acquisition started again.

2.4 Validation

The experimental procedure and the detection techniques were validated with pure carbon dioxide and compared with the commercial software REFPROP-NIST. Table 1 shows the saturation pressure for pure CO_2 measured by this work's apparatus (visual and acoustic technique) and the reference values. The deviation was calculated using Eq. (1).

$$D = \frac{P_{\exp} - P_M}{P_M} \qquad (1)$$

Table 1. Experimental validation with pure CO_2.

Temperature [K]	Visual [MPa]	Deviation %	Acoustic [MPa]	Deviation %	REFPROP [MPa]
283.15	4.5214	0.4265	4.4557	-1.0326	4.5022

288.65	5.1187	-0.5827	5.1785	0.5788	5.1487
293.15	5.7527	0.4119	5.8254	1.6809	5.7291
299.65	6.6940	0.5181	6.7278	1.0255	6.6595
303.05	7.2491	0.7211	7.1961	-0.0153	7.1972

The visual technique consists in record the experiment and detect visually the nucleation of the first liquid drop inside the equilibrium cell. Figure 3 shows the moment that the first liquid drop can be visually detected in the cell.

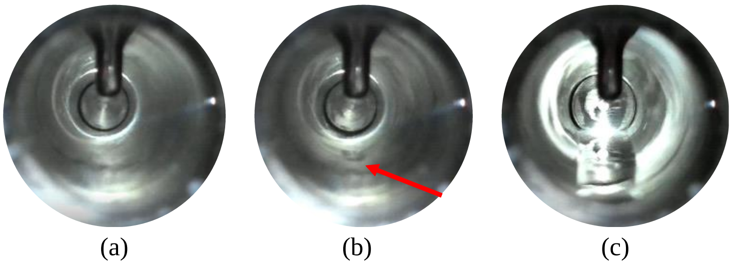


Figure 3. Visual detection of liquid nucleation for pure CO_2.

The acoustic technique measures the energy of the mechanical wave. As shown by (Miguel Jr, 2020) and (Cardozo, 2011) there is a discontinuity in the energy at the moment of the phase transition. Kordikowski et al. (1996) have showed that the velocity of propagation of the wave also have a discontinuity in the moment of the phase transition, resulting in a discontinuity in the energy. This study noticed the discontinuity in the energy, as can be seen in Figure 4.

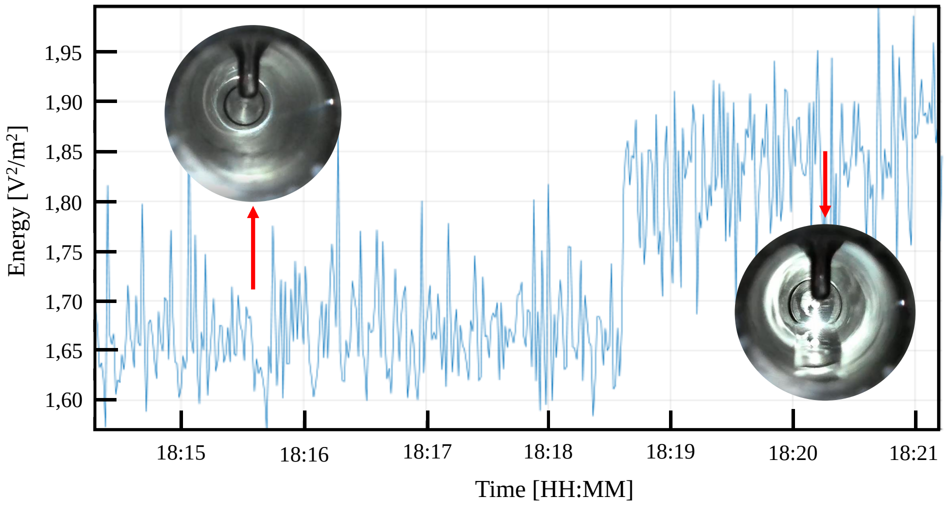


Figure 4. Energy versus time plot for the acoustic measurement. Experiment carried with pure CO_2.

3. RESULTS AND DISCUSSION

Table 2 shows the experimental results for both techniques, where y_{CH4} is the molar fraction of methane in gaseous phase, P_v is the pressure obtained by the visual technique and P_{US} is the pressure obtained by the ultrasonic measurements.

Table 2. Experimental results for acoustic and visual techniques.

y_{CH4}	P_v [MPa]	P_{US} [MPa]
	313.15 K	
0.9824	1.226	1.267
0.9876	1.666	1.560
0.9898	1.986	2.062

0.9925	2.998	3.095
	323.15 K	
0.9768	1.549	1.554
0.9823	1.903	-
0.9892	4.004	3.963
0.9897	4.175	4.168
0.9901	4.439	4.407
	333.15 K	
0.9708	1.963	1.958
0.9765	2.442	2.377
0.9804	3.340	3.371
0.9830	4.043	3.947
0.9857	5.611	4.865
	343.15 K	
0.9579	2.378	2.245
0.9661	2.905	2.882
0.9728	3.497	3.445
0.9774	4.656	4.542
0.9828	8.569	8.546
	353.15 K	
0.9328	2.034	2.076
0.9542	3.081	3.044
0.9629	4.197	3.933
0.9658	4.660	4.665
0.9708	6.219	6.239
0.9736	7.336	7.342

The results in Table 1 shows good agreement between the visual technique and the acoustic technique. Most of experimental points have a lower dew point pressure for the acoustic technique. This happens because the liquid drop must be above certain volume to be visible. Consequently, when the viewer detect the liquid drop the system is a little pass the dew point. The acoustic technique, on the other hand, is sensible to changes in the compressibility in the moment of the nucleation of a new phase. For this reason, the ultrasonic measurements are considered more reliable than the visual technique and is compared against the commercial software for thermodynamic prediction Multiflash, shown is Figure 5.

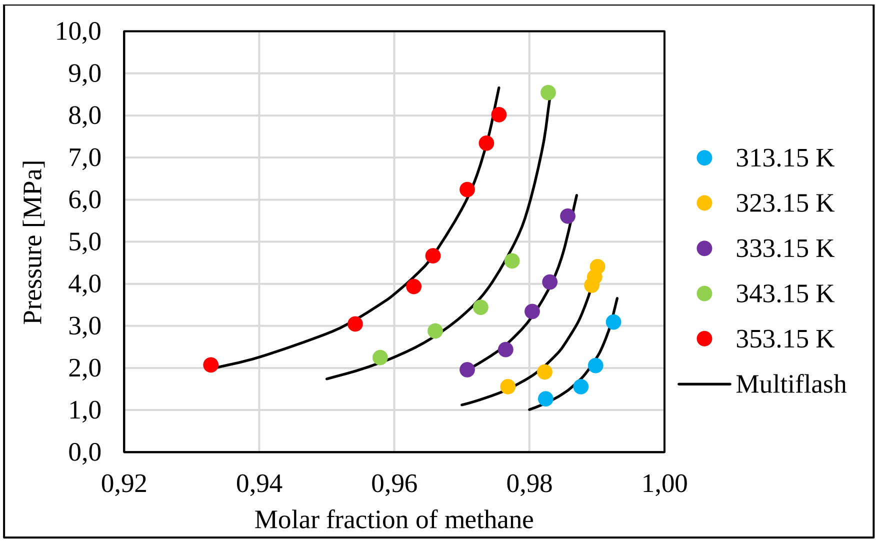


Figure 5. Experimental results compared with Multiflash.

There are data available in the literature for the temperatures of 313.15 K 323.15 K and 333.15 K. Figure 6 shows the comparison between data from this work and the data available in the literature.

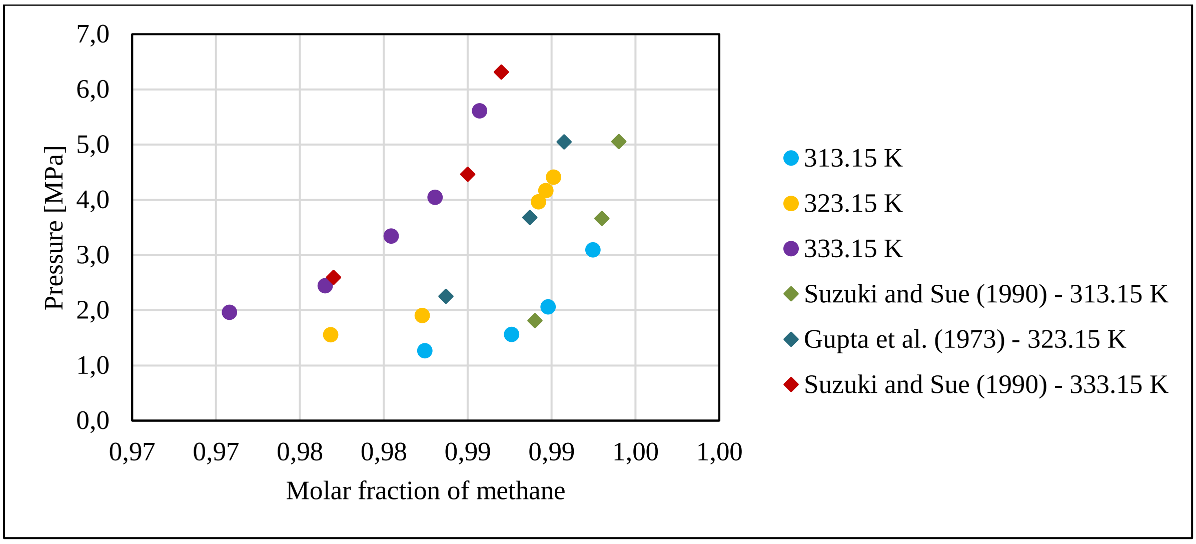


Figure 6. This work experimental data and literature experimental data.

As can be seen in Figure 6, this work's data is follows the same tendencies than the literature data. Therefore, this work provides more consistent data for the literature in a wider range of temperatures and compositions.

4. CONCLUSIONS

Liquid-vapor equilibrium (ELV) for the methane + ethanol system have been studied by some authors, but usually only the bubble point is addressed. This work provides more data about the dew point about this system in other to enhance the prediction performance of thermodynamic models and be applicable to the industry.

Between the two techniques applied in this work, the acoustic is more reliable since it is not attached to the viewer's ability, and it can expand the applicability of the synthetic method. It is applicable in cells without windows, making it possible to perform experiments at high pressures.

Dew point data is scarce in the literature, and it usually is carried by the analytic method, applying a gas chromatograph. This study shows a cheaper solution to perform dew point experiments applying a synthetic method, presenting results that are consistent with literature data and with commercial thermodynamic models.

5. ACKNOWLEDGEMENTS

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