COBEM 2023 27TH INTERNATIONAL CONGRESS OF MECHANICAL ENGENEERING

ABCM Brazilian Society of Mechanical Sciences and Engineering
27th ABCM International Congress of Mechanical Engineering
December 04-08, 2023, Florianópolis-SC, Brazil

COB-2023-0551
EXPERIMENTAL AND THEORETICAL CHARACTERIZATION OF THERMOPHYSICAL PROPERTIES AND ELECTRICAL PERMITTIVITY OF CO_2 AND DODECANE MIXTURES

Erich T. Tiuman
Jean P. N. Longo
Felipe K. Marozo
David Sena Kabacznik
Eduardo N. dos Santos
Rigoberto E. M. Morales
Moisés A. Marcelino Neto
Multiphase Flow Research Center (NUEM), Federal University of Technology – Paraná (UTFPR). Rua Deputado Heitor Alencar Furtado 5000, Bloco N, CEP 81280-340, Curitiba, Brazil
erich_tiuman@hotmail.com, jeanplongo@gmail.com, kneip.felipe@gmail.com, davidsena@alunos.utfpr.edu.br, ensantos@utfpr.edu.br, rmorales@utfpr.edu.br, mneto@utfpr.edu.br

Marco J. da Silva
Institute of Measurement Technology, Johannes Kepler University Linz. Altenberger Str. 69, 4040 Linz, Áustria.
mdasilva@utfpr.edu.br

Abstract. *Multiphase flow meter (MPFM) is a device used to measure the flow rate of multiple fluids in a single pipe. It is an important tool for measuring the production, distribution and consumption of oil and gas in an efficient manner. All current MPFMs require accurate fluid properties as part of their PVT (pressure, volume and temperature) configuration in order to deliver accurate flow rate of production fluids. Due to recent discoveries of pre-salt and its characteristics of having a high content of carbon dioxide the need of evaluating the performance of nowadays technologies related to flow meters' behavior in presence of high content of* CO_2 *was created. For this reason, investigating the impact of carbon dioxide content in the thermophysical properties of a multiphase mixture and consequently also the impact in the performance of flow meters has received much attention these days. In this work, it was conducted an experimental and theoretical study of thermophysical properties (electrical permittivity, density, solubility and viscosity) of a mixture composed by dodecane and carbon dioxide, as model fluids. A test bench has been developed with a circuit for circulation of the mixture and measurements of the properties aforementioned. This test bench operates with a range of temperature from 5 to 80°C, pressure from 1 to 170 bar and content of* CO_2 *from 0 to 100%. The theoretical study was an implementation and calibration of an equation of state (EoS) using the experimental data obtained from the test bench. With all these experimental and theorical study it was possible to evaluate the influence of carbon dioxide content on parameters of solubility, viscosity, electrical permittivity and density.*

Keywords: *Multiphase Flow Metering, Equation of State, Carbon Dioxide, Thermodynamics*

1. INTRODUCTION

In oil fields, the utilization of Multiphase Flow Meters (MPFMs) is crucial for reservoir management and maximizing oil and gas production (Meribout et al., 2020). MPFMs play a significant role in accurately measuring the flow rates of oil, gas, and water simultaneously within a production well. By providing real-time data on the composition and flow rates of the multiphase fluids, MPFMs enable operators to make informed decisions regarding reservoir management strategies, production optimization, and allocation of resources. Besides that, the use of MPFMs reduces hardware needed for onshore and offshore applications due to the removal of a dedicated test separator for well testing applications (Falcone et al., 2002). A MPFM is represented schematically by Figure *1*.

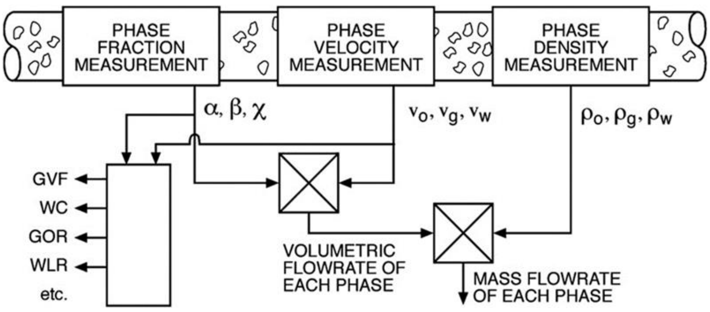

Figure 1. The determination of the mass flow rates of oil, gas and water demands the characterization of two-phase fractions, three velocities and three phase densities. Source: Thorn et al. (2013).

The recent discoveries of pre-salt reservoirs, known for their high carbon dioxide (CO_2) content (de Freitas et al., 2022), have prompted the need to evaluate the performance of modern flow meter technologies in the presence of such elevated CO_2 levels. Therefore, there is currently significant attention being given to investigating the influence of carbon dioxide content on the thermophysical properties of multiphase mixtures, as well as its subsequent impact on flow meter performance.

The aim of this study is to conduct an experimental and theoretical investigation into the influence of dissolved CO_2 quantity in the liquid phase of a CO_2 and dodecane mixture. The focus is on understanding how this affects the thermophysical and electrical properties of the mixture, with the ultimate goal of exploring the impact of these property variations on Multiphase Flow Meters (MPFM) measurements.

The experiments were carried out by varying pressure (1 to 170 bar) and temperature (5 to 80°C), which in turn influenced the solubility of CO_2 (ranging from 0 to 100%). This allowed for the analysis of the latter parameter's influence on the viscosity, density, and electrical permittivity of the liquid phase in the mixture.

A thermodynamic model, employing the Cubic Plus Association (CPA) equation of state, was applied and implemented for comparison with the experimental results obtained.

2. METHODOLOGY

This chapter presents information about the experimental setup and how the experiments are conducted, as well as the mathematical modeling and the implementation of the equation of state that will provide all necessary properties.

2.1 Experimental methodology

The experimental setup was designed and built to assess the influence of CO_2 on the thermophysical properties (viscosity, solubility, density and electrical permittivity) of a fluid. In the present work, n-dodecane was used as the working fluid. The experimental setup developed and used throughout the experimental phase is described below:

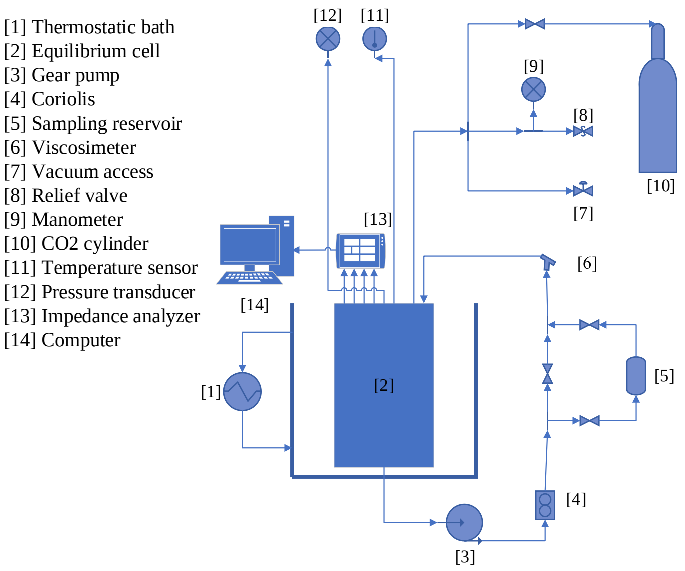

Figure 2. Schematic Test Bench

Figure 2 shows the schematic of the rig with which all the experimental data were obtained. The thermostatic bath [1] was used to regulate the cell temperature [2] during the experiments when the mixture reached equilibrium prior to being conveyed through the entire loop via a gear pump [3]. The mixture density is determined by the Coriolis flow meter [4]. Then, the mixture was directed to the sampling reservoir [5], where its solubility was measured through gravimetry before proceeding to the viscosimeter [6], where its viscosity was determined. Subsequently, the mixture was returned to the cell and the loop was restarted. In addition to the properties line, a separate line feeds the cell with the components that compose the mixture. The vacuum line [7] removes air from the cell, while [8] serves as a relief valve ensuring the safety of the equipment and a CO2 cylinder [10] is used to pressurize the CO_2-dodecane mixture. A temperature sensor [11] and a pressure transducer [12] are used to monitor the temperature and pressure of the mixture during the experiment. The electrical permittivity was evaluated by means of an impedance analyzer [13] connected to an electrical permittivity sensor, which assessed this property in the mixture. The acquisition of all measured properties was facilitated through a computer [14].

2.2 Thermodynamic modeling

In order to model all the necessary properties, the first step in numerical development is the application of an equation of state, whose solution provides the molar specific volume of the fluid. The density can be obtained by dividing the molar mass of the fluid by the molar specific volume. The CPA equation of state was chosen. This EoS is composed of three terms, the first two representing the same formulation as the SRK (Soave-Redlich-Kwong). These terms represent the ideal portion, derived from the theory of perfect gases and the corrections due to the van der Waals forces of attraction and repulsion. The last term comes from statistical thermodynamics and describes the associating bonds of the substances (Kontogeorgis & Folas, 2010). The CPA can be written according to the pressure-explicit Eq. (1). An iterative calculation (Newton-Raphson method) yields the molar specific volume when convergence is reached.

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)} - \frac{1}{2}\frac{RT}{v}\left(1 - \frac{v^2}{g}\frac{\partial g}{\partial v}\right)\sum_i \sum_{A_i}\left(1 - X_{A_i}\right) \tag{1}$$

where R is the ideal gas constant, T is temperature, v is the molar specific volume, b is a CPA constant, a(T) is the attraction parameter, g is the radial distribution parameter, and X_{Ai} is the fraction of unassociated associating sites.

This equation of state was used as the basis for calculating the other properties, through the application NUEMPROP developed by Pereira (2022), that will be presented in the results section along with the experimental data obtained from the experimental setup. The properties of density, viscosity, electrical permittivity, and solubility were obtained through additional calculations performed in conjunction with CPA.

3. RESULTS

This section will provide a presentation of all the results obtained, including those acquired through experiments and modeling.

3.1 Experimental results

Firstly, the equilibrium curve between CO_2 and n-dodecane is presented. The curves represent the maximum solubility of CO_2 in n-dodecane for a given temperature. Figure 3 shows the pressure as a function of the CO_2 solubility in n-dodecane for different isotherms. It can be observed that the pressure increases with the increase in the amount of CO_2 solubilized in the mixture. Furthermore, the temperature tends to increase the pressure alongside the amount of CO_2 solubilized. That is, the higher the temperature, the higher the system's pressure. Finally, it is observed that only the first two curves reach 100% CO_2 solubility. This is because above 35°C, CO_2 is already in the supercritical state, and therefore its conditions cannot be evaluated.

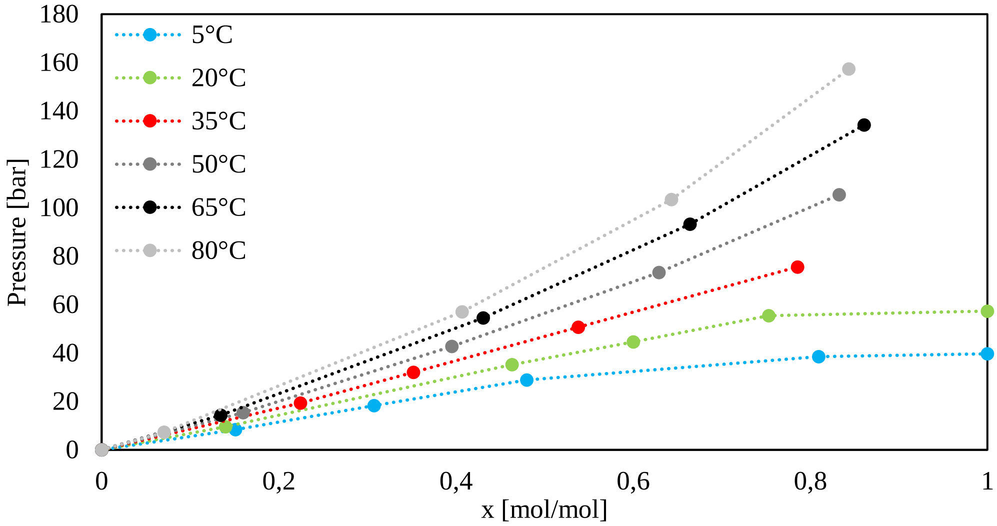

Figure 3. Equilibrium curve CO_2 + Dodecane.

In addition to the equilibrium curve, the viscosity and density curves were also evaluated. Figure 4 presents the viscosity as a function of the CO_2 solubility in n-dodecane for different temperatures. As it can be observed, the viscosity tends to decrease with increasing temperatures, a behavior common to many substances. However, the increase in the amount of CO_2 causes a significant decrease in viscosity. For example, a reduction of approximately 50% in viscosity is observed for 50% solubility at 5ºC when compared with pure n-dodecane. This result shows the importance of the CO_2 solubility in the oil.

Figure 5 shows the density as a function of the CO_2 solubility in n-dodecane for different temperatures. It can be observed that the density is reduced by increasing temperature. Moreover, in most cases, an increase in the amount of CO_2 causes an increase in the density of the mixture. This is because CO_2 in the liquid phase is denser than n-dodecane under the same pressure and temperature conditions. Therefore, an increase in the amount of CO_2 in the mixture will cause a slight increase in density, as it can be seen in Figure 5.

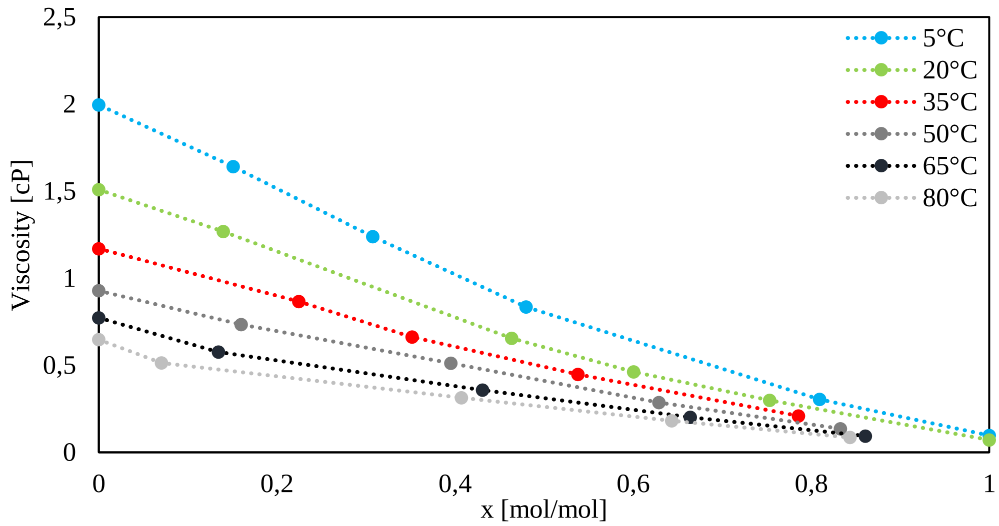

Figure 4. Viscosity as a function of the CO_2 solubility in n-dodecane.

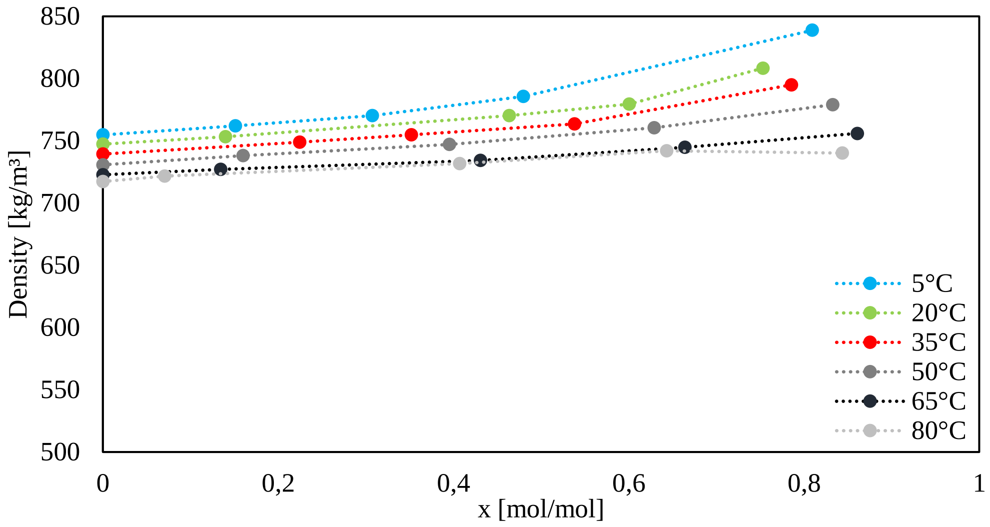

Figure 5. Density as a function of the CO_2 solubility in n-dodecane

Regarding to the electrical permittivity, the first two isotherms (5 ºC and 35 ºC) were tested and the results proved to be promising upon exhibiting satisfactory trends, the electrical permittivity of the mixture tends to decrease with increasing CO_2 solubility. It is caused because the CO_2's electrical permittivity is lower than the dodecane's one for the same conditions, this can be observed in Figure 6.

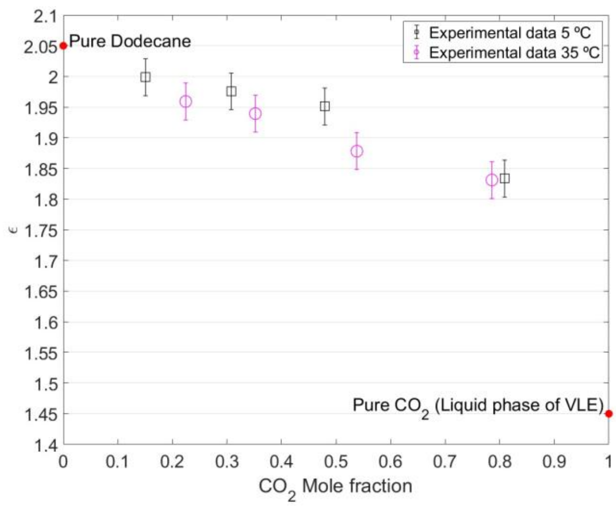

Figure 6. Experimental data for permittivity measurements for 5 ºC and 35 ºC.

3.2 Thermodynamic modeling results

After evaluating all the properties for the simplest cases and verifying that the thermodynamic model provides reliable results, the influence of the CO_2 on the mixture density, viscosity and solubility was evaluated.

Figure 7 presents curves of pressure as a function of the solubility for different temperatures obtained experimentally and through the CPA model. It can be observed that the curves obtained by the CPA EoS have the same trend as the experimental results. Figure 8 compares the experimental and the CPA model solubilities for different temperatures. The continuous black line corresponds to a perfect match between experimental and modeled values, while the dashed lines represent ± 10% of deviation. It can be observed that several points lie inside the ± 10% region after the optimization of binary interaction parameter (k_{ij}) which represents a good agreement between experimental and modeling.

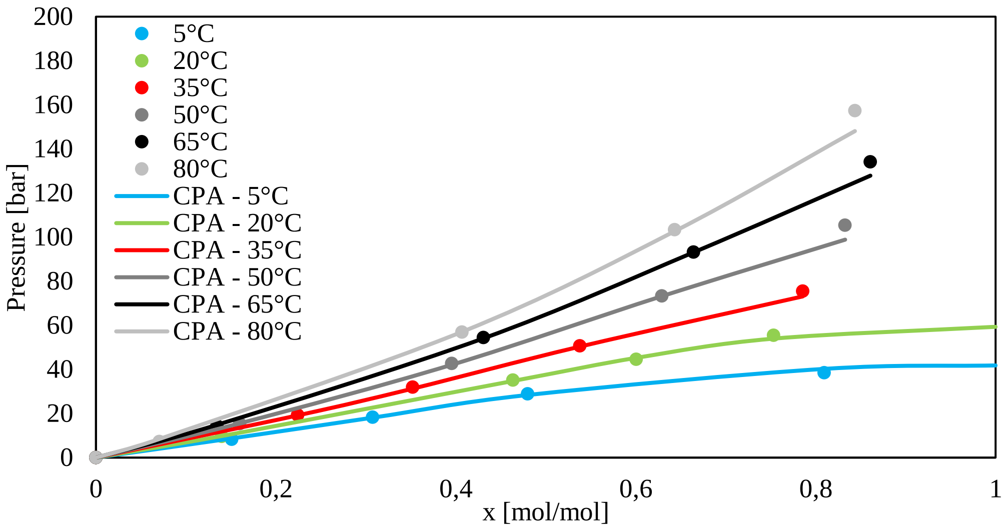

Figure 7. CPA model equilibrium curve for CO_2 + n-dodecane plotted with experimental points

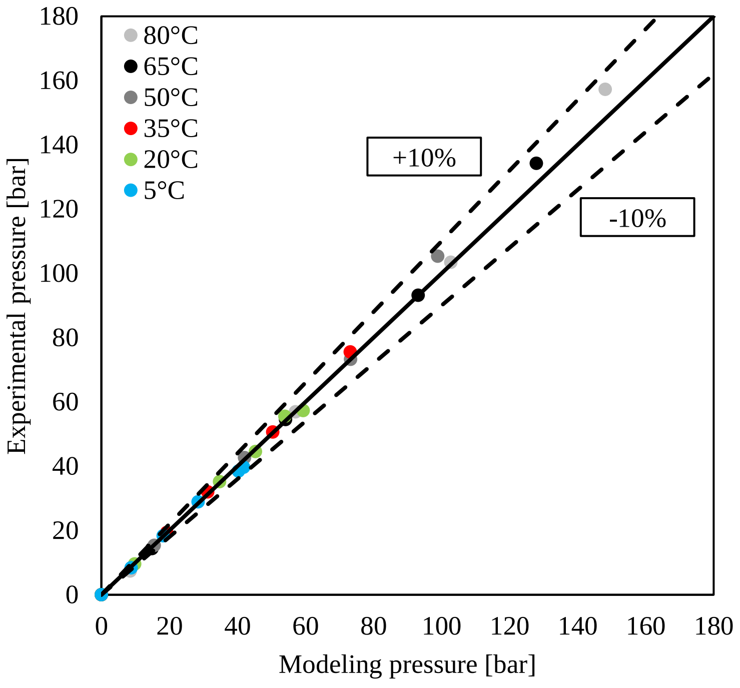

Figure 8. Comparison between experimental and CPA model pressure for different temperatures.

Figure 9 presents the viscosity as a function of the solubility for both different temperatures calculated through the CPA model and the ones obtained experimentally. The CPA model and the experimental data show the same trend, that is, the reduction in viscosity by increasing the CO_2 solubility in n-dodecane, as seen in Figure 9. Figure 10 compares modeled and experimental viscosity data for different temperatures. Because of the lower viscosity values and the f-theory model used, several points lie outside the ±10% region. Besides the behavior of the property is the same for modeling and experimental data, it can be seen that the model is not completely satisfactory for this application. In this case, another model should be implemented to lower the average error between model and experimental data.

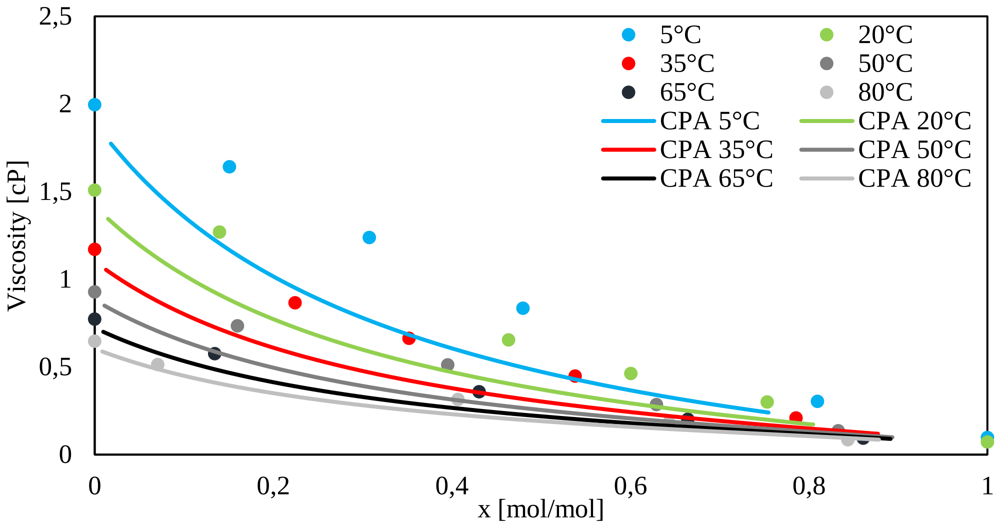

Figure 9. CPA model viscosity curve for CO_2 + dodecane plotted with experimental points.

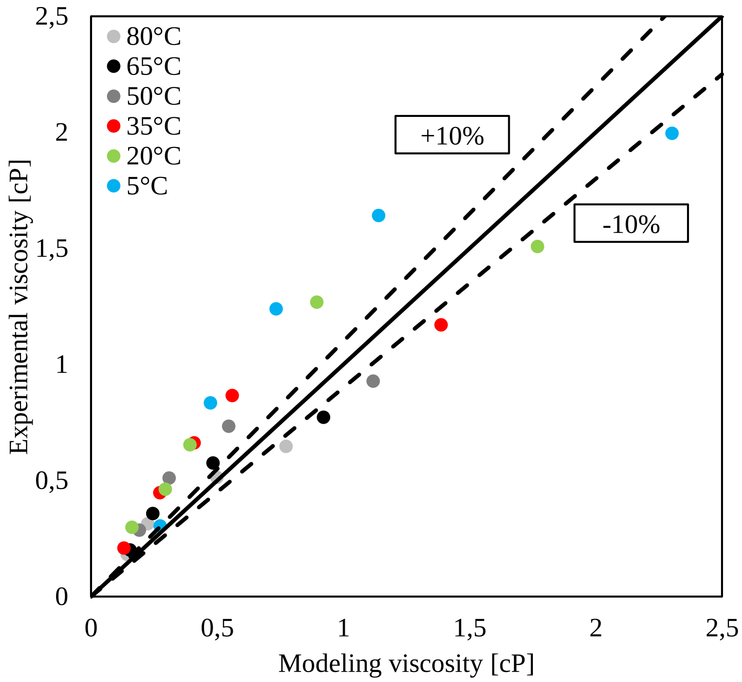

Figure 10. Comparison between experimental data and CPA model viscosities for different temperatures.

Figure 11 shows the density as a function of the CO_2 solubility in n-dodecane obtained both experimentally and through the thermodynamic model. The thermodynamic model predicted the behavior of density well, as for the previous variables. Figure 12 compares the experimental and model values for the density at different temperatures. It can be observed that the density values calculated by the CPA model are within the ± 10% region, showing good agreement with the experimental results.

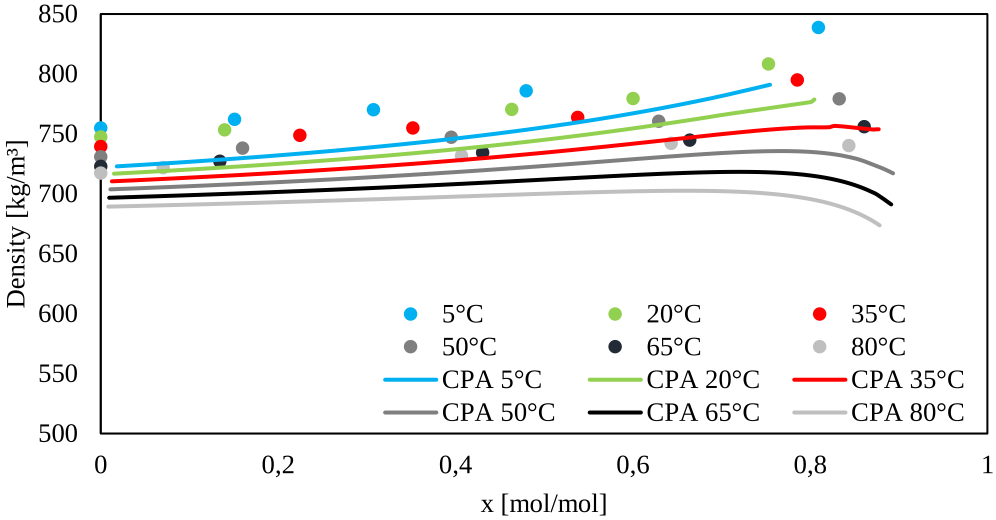

Figure 11. CPA model density curve for CO_2 + n-dodecane plotted with experimental points.

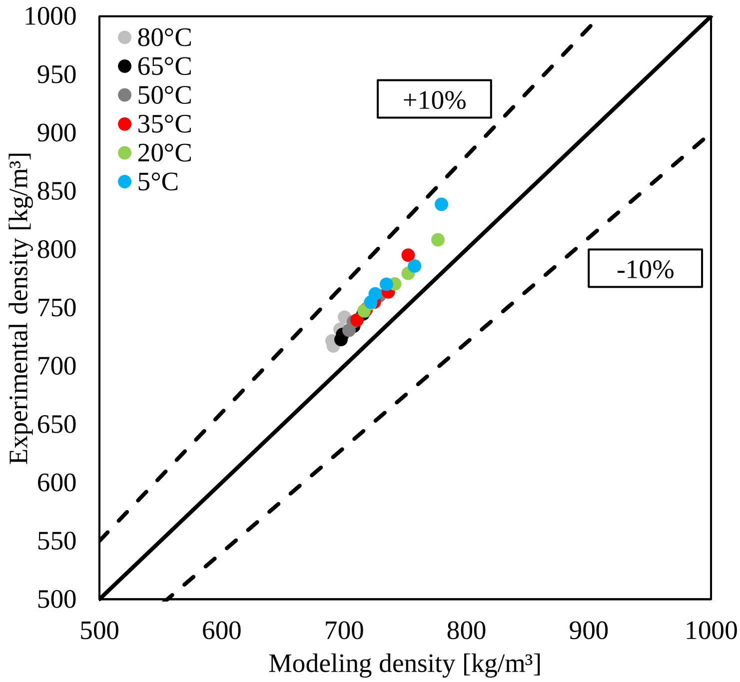

Figure 12. Comparison between experimental data and CPA model densities for different temperatures.

In Figure 13, the relationship between electrical permittivity and CO_2 solubility in n-dodecane is presented, showcasing both experimental data and predictions obtained through the thermodynamic model. The model exhibited accurate predictions of the electrical permittivity, consistent with the performance observed for previous variables. Figure 14 further examines the comparison between experimental and model-derived values for electrical permittivity across various temperatures. Notably, the results demonstrate that the electrical permittivity values calculated by the CPA model fall within the ±10% range, indicating favorable agreement with the experimental findings.

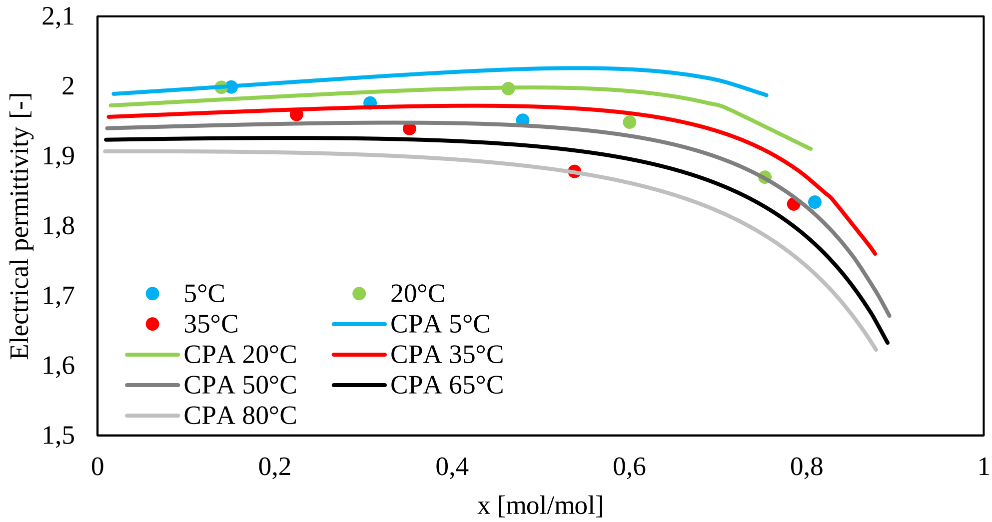

Figure 13. CPA model electrical permittivity curve for CO_2 + n-dodecane plotted with experimental points.

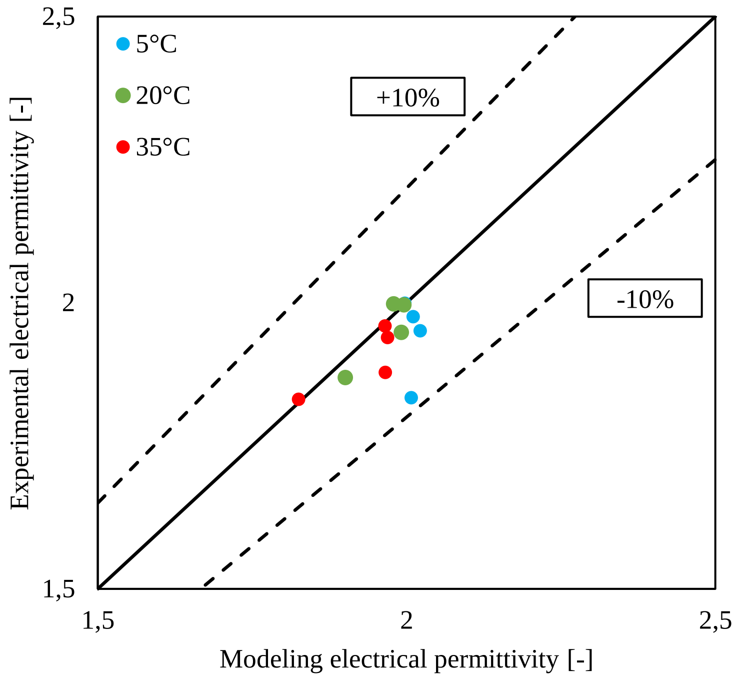

Figure 14. Comparison between experimental data and CPA model electrical permittivity for different temperatures.

4. CONCLUSIONS

This study focused on examining the impact of dissolved CO_2 in a CO_2 and dodecane mixture on the thermophysical and electrical properties, with specific emphasis on their influence on Multiphase Flow Meters (MPFMs) used in oil fields. Experimental investigations involved varying pressure and temperature to analyze CO_2 solubility's effect on viscosity, density, and electrical permittivity. A thermodynamic model based on the Cubic Plus Association (CPA) equation of state was applied for comparison. The experimental setup comprised a thermostatic bath, gear pump, Coriolis flow meter, sampling reservoir, viscosimeter, and impedance analyzer. Results showed that increasing CO_2 solubility raised pressure and reduced viscosity. Density increased with higher CO_2 solubilization, while electrical permittivity decreased. The CPA model provided reliable predictions, closely aligning with experimental data and those results were improved by optimizing the k_{ij} parameter for the mixture presented. By understanding the effects of dissolved CO_2 on properties and its influence on MPFMs, it is possible to make informed decisions for maximizing oil and gas production.

5. ACKNOWLEDGEMENTS

The authors acknowledge the SHELL BRASIL PETRÓLEO LTDA. for the financial support under the Grant No. CW499828.

6. REFERENCES

de Freitas, V. A., Vital, J. C. dos S., Rodrigues, B. R., & Rodrigues, R. (2022). Source rock potential, main depocenters, and CO2 occurrence in the pre-salt section of Santos Basin, southeast Brazil. *Journal of South American Earth Sciences*, *115*, 103760. https://doi.org/10.1016/j.jsames.2022.103760

Falcone, G., Hewitt, G. F., Alimonti, C., & Harrison, B. (2002). Multiphase Flow Metering: Current Trends and Future Developments. *Journal of Petroleum Technology*, *54*(04), 77–84. https://doi.org/10.2118/74689-JPT

Kontogeorgis, G. M., & Folas, G. K. (2010). *Thermodynamic Models for Industrial Applications*. Wiley. https://doi.org/10.1002/9780470747537

Meribout, M., Azzi, A., Ghendour, N., Kharoua, N., Khezzar, L., & AlHosani, E. (2020). Multiphase Flow Meters Targeting Oil & Gas Industries. *Measurement*, *165*, 108111. https://doi.org/10.1016/j.measurement.2020.108111

Pereira, M. (2022). *Caracterização termodinâmica de misturas ricas em dióxido de carbono* [M.Sc. Thesis]. Universidade Tecnológica Federal do Paraná.

Thorn, R., Johansen, G. A., & Hjertaker, B. T. (2013). Three-phase flow measurement in the petroleum industry. *Measurement Science and Technology*, *24*(1), 012003. https://doi.org/10.1088/0957-0233/24/1/012003

7. RESPONSIBILITY NOTICE

The authors are the only responsible for the printed material included in this paper.