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THERMOPHYSICAL PROPERTIES FOR CO_2 AND CO_2 RICH MIXTURES PREDICTED USING A CPA EOS

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Abstract. *In order to project or evaluate the operational parameters for systems involving injection or reinjection of* CO_2 *it is essential to know the main state properties as well as the transport properties of the fluid concerned. Particularly for applications on the oil and gas industry it is crucial not only access the properties for pure carbon dioxide but also for a great range of mixtures contemplating the natural impurities often found alongside this substance. Once the value of most of the thermophysical proprieties are strongly affected by the composition of the fluid and the conditions of temperature and pressure it is interesting to explore methods to predict these properties applying an equation of state (EoS) which has the same inputs. One of the most commonly tested EoS for such activities are the cubic equations of state. These equations are simple and often demand no more than critical proprieties for its operation. Also, these EoS are well known for being appropriate for modeling systems with hydrocarbons, as well as other simple nonpolar substances as carbon dioxide. However, these equations do not wield good results when applied for polar fluids, such as water, therefore an addition of an associative term to the model is necessary hence the Cubic Plus Association EoS was chosen. In this present work the properties specific mass, enthalpy, entropy, and specific heat were calculated using CPA to* CO_2 *rich mixtures involving methane, propane, nitrogen and water for temperatures and pressures ranging from 250 to 600 K and 10 to 700 bar, respectively. The ranges of pressure and temperature were chosen based on the conditions found on the industry of oil and gas. The results were compared with experimental correlated data and it was observed that the average deviation was in a satisfactory level for the proposed application.*

Keywords: *CPA,* CO_2 *rich mixtures, Thermophysical properties, Oil and Gas industry*

1. INTRODUCTION

During the extraction of petroleum many subproducts with little or no commercial value are obtained along the oil. These substances are separated soon after and each are given the adequate discharge. The carbon dioxide, or rather mixtures rich in carbon dioxide, are one of these subproducts. Due to its role in the greenhouse effect, the CO_2 cannot be freely released in the atmosphere. One of the most beneficial alternatives to its discharge is the reinjection of these mixtures into the reservoir. Fortunately this processes also facilitate the extraction of petroleum through rising the pressure inside the reservoir and also diminishing the viscosity of the remaining oil (Fujieda and Iwamoto, 2016). This process of reinjection of CO_2 can also be classified as an enhanced method of oil recovery (Thomas, 2001), that is an advanced process that possibilities more oil being produced from the same reservoir.

In order to implement such a process, it is necessary to evaluate the main state and transport properties of the fluids involved. These properties are applied in simulations, studies of optimization of operational conditions and to predict circumstances which multiphase flow may occur. Due to the great interest in suitable ways to discharge CO_2 plus the interest in enhanced methods of recovery many studies, experimental and numerical, have been conducted in the latest years (Li *et al.*, 2011).

Given the severe conditions in which the reinjection of CO_2 is made, it becomes attractive to apply comprehensive thermodynamic models to predict its state and transport properties. One on the main approach used to this end is the employment of an equation of state for the prediction of the specific volume and departure functions for modeling the residual properties of state as enthalpy and entropy.

Many EoS can be applied to model CO_2 rich mixtures. Some equations of high complexity such as GERG-2008, virial equations and its variants have been used by many authors (Lee and Kesler, 1975; Al-Sahhaf, Kidnay and Sloan, 1983; Thiery, Vidal and Dubessy, 1994; Westman *et al.*, 2016). These equations usually produce results with low deviations, but they are depended on many constants that demand calibration made through a large amount of experimental data.

One alternative worth consideration are the cubic equations of state. This class of equations derives from the van der Waals equation and take account the ideal behavior of the fluid plus the interaction of attraction and repulsion among the molecules. Many variations such as the Peng Robinson and the Soave-Redlich-Kwong have been explored extensively in the literature. These equations have only three component dependent constant, and these parameters can be estimated from the critical point plus the acentric factor(Smith, J. M.; Van Ness, H. C.; Abbot, 2007). The simplicity of this class of equations make them useful for industrial appliances (Li *et al.*, 2011).

Studies shown that the cubic EoS can produce results with good correlation compared to experimental data (Al-Sahhaf, 1990; Thiery, Vidal and Dubessy, 1994). Even for derivate properties such as Joule-Thomson coefficient this approach has proven to be suitable, with average deviations below 10% for systems with carbon dioxide, nitrogen and hydrocarbons (Rocha *et al.*, 2016).

One of the main limitations of the cubic EoS is when modeling systems with one or more associating substances. As the water properties are strongly influenced by association forces it is important to have it taken in account. It is also important to point that water is usually present, even though in small fractions, in the CO_2 mixtures that are reinjected. In this context the CPA EoS (Cubic Plus Association) is a viable option since it combines the simplicity of the cubic EoS plus a term capable of modeling the influence of the associating forces (Kontogeorgis and Folas, 2009).

The aim of this work is to apply the CPA EoS plus departure functions to evaluate the specific volume, enthalpy, entropy, specific heat and Joule-Thomson coefficient for mixtures with large molar fractions of CO_2 plus a contaminant such as water, nitrogen or a hydrocarbon. The results were then compared with correlated data.

2. METHODOLOGY

This section presents the procedure applied to calculate the proposed properties. It is divided in two subsections, the first concerns the CPA EoS and its constants. The specific volume is obtained from the EoS. The second describe the departure functions used to calculate the enthalpy, entropy, specific heat and Joule-Thomson coefficient.

2.1 CPA EoS

The CPA EoS were implemented as presented in Kontogeorgis and Folas (2009). The equation is explicit in pressure as:

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

Where X_{A_i} represents the fraction of free-associating sites of the kind *A* of the component *i*. g is the radial distribution function, v is the molar specific volume, T is the temperature, p is the fluid pressure, R is the universal gas constant, b is a CPA constant and $a(T)$ is a CPA parameter calculate as:

$$a(T)=a_0\left(1+c_1\left(1-\sqrt{T_r}\right)\right)^2 \tag{2}$$

Where T_r is the reduced temperature, a_0 and c_1 are CPA pure substance constants. The following mixing rules are applied:

$$a_m=\sum_i\sum_j x_i x_j\sqrt{a_i a_j}\left(1-k_{ij}\right) \tag{3}$$

$$b_m=\sum_i b_i x_i$$

Where the subscript m denotates mixture constants and x_i corresponds to the molar fraction of the compound *i* in the mixture. k_{ij} is the binary adjusted mixing parameter. The values utilized for this parameter are shown in Table 2.

The radial distribution can be obtained as:

$$g = \frac{4v}{4v - 1.9b} \tag{4}$$

The water associating scheme considered in this paper is 4C, as suggested by Kontogeorgis and Folas (2009). The fraction of free-associating sites is calculated as:

$$X_{A_i} = \frac{1}{1 + \frac{1}{v}\sum_{j} x_j \sum_{B_j} X_{B_j} \Delta^{A_i B_j}} \tag{5}$$

Where $\Delta^{A_i B_j}$ is the associating strength calculated as:

$$\Delta^{A_i B_j} = g\left[e^{\left(\frac{\varepsilon^{A_i B_j}}{RT}\right)} - 1\right] b_{ij} \beta^{A_i B_j} \tag{6}$$

$\varepsilon^{A_i B_j}$ is the association energy, $\beta^{A_i B_j}$ is the association volume and b_{ij} is a binary parameter calculated as:

$$b_{ij} = \frac{b_i + b_j}{2} \tag{7}$$

The association energy and association volume are constants obtained from the literature for pure substances. For mixture calculations these parameters obey the following mixing rules:

$$\varepsilon^{A_i B_j} = \frac{\varepsilon^{A_i B_i} + \varepsilon^{A_j B_j}}{2} \tag{8}$$

$$\beta^{A_i B_j} = \sqrt{\beta^{A_i B_i} \beta^{A_j B_j}} \tag{9}$$

With the inputs of pressure, temperature and composition, plus the constants for pure substances informed in the Table 1 the Eq. (1) can be solved numerically, finding the value of specific molar volume.

Table 1. CPA pure substances constants.

Substance	**a0 [bar L^2 mol^{-2}]**	**b [L mol−1]**	**c1 [-]**	**ε [bar L mol−1]**	**B [-]**
methane (1)	2.3203	0.0291	0.4472	-	-
propane (2)	9.1188	0.0578	0.6307	-	-
water (2)	1.2277	0.0145	0.6736	166.55	0.069
nitrogen (3)	1.3660	0.0262	0.5185	-	-
carbon dioxide (4)	1.1856	0.0284	0.6600	-	-

(1) Tzirakis, Karakatsani and Kontogeorgis, 2016
(2) Dilay and Heidemann, 1986
(3) Khosharay, 2015
(4) Bjørner and Kontogeorgis, 2016

Table 2. Binary adjusted mixing parameters.

System	**k_{ij}**
CO_2/CH_4 (1)	0.09827
CO_2/N_2 (1)	-0.02800
CO_2/C_3H_8 (2)	0.13100

(1) Abbas et al., 2011

(2) Xu et al., 2019

2.2 Departure Functions

The other properties were calculated through departure functions. For enthalpy, entropy and specific heat, the full value of each property was obtained as the sum of the ideal parcel plus the residual property. The ideal parcels were calculated as correlations dependent on temperature only as proposed in NIST Webbook (2021). The residual properties were determined through derivations of the Helmholtz free energy. The total energy can be determined as a sum of the non-associative and associative parcels as follows:

$$F=-\ln\left(1-\frac{b}{v}\right)-\frac{a(T)}{RTb}\ln\left(1+\frac{b}{v}\right) \tag{10}$$

$$Q=\sum_i n_i\sum_{A_i}\left(\ln X_{A_i}-\frac{1}{2}X_{A_i}+\frac{1}{2}\right) \tag{11}$$

Where F and Q are respectively the non-associative and associative parcel of the Helmholtz free energy and n_i is the number of mols of the substance *i* in the mixture. All the other parameters are the same used on the CPA EoS.

The residual properties and the Joule-Thomson coefficient are calculated as:

$$h^R=RT^2\left(\frac{\partial F}{\partial T}+\frac{\partial Q}{\partial T}\right)_{v,n}+pv-nRT \tag{12}$$

$$s^R=-RT\left(\frac{\partial F}{\partial T}+\frac{\partial Q}{\partial T}\right)_{v,n}-RF+nR\ln\left(\frac{pv}{RT}\right) \tag{13}$$

$$C_v^R=-RT^2\left(\frac{\partial^2 F}{\partial T^2}+\frac{\partial^2 Q}{\partial T^2}\right)_{v,n}-2RT\left(\frac{\partial F}{\partial T}+\frac{\partial Q}{\partial T}\right)_{v,n} \tag{14}$$

$$\left(\frac{\partial p}{\partial v}\right)_{T,n}=-RT\left(\frac{\partial^2 F}{\partial v^2}+\frac{\partial^2 Q}{\partial v^2}\right)_{T,n}-\frac{nRT}{v^2} \tag{15}$$

$$\left(\frac{\partial p}{\partial T}\right)_{v,n}=-RT\left(\frac{\partial^2 F}{\partial T\partial v}+\frac{\partial^2 Q}{\partial T\partial v}\right)_{n}+\frac{p}{T} \tag{16}$$

$$C_p^R=C_v^R-T\frac{\left(\frac{\partial p}{\partial T}\right)_{v,n}^2}{\left(\frac{\partial p}{\partial v}\right)_{v,n}}-Rn \tag{17}$$

$$\mu_{JT} = -\frac{1}{C_p}\left[v + T\frac{\left(\frac{\partial p}{\partial T}\right)_{v,n}}{\left(\frac{\partial p}{\partial v}\right)_{T,n}} \right] \tag{18}$$

Where h^R, s^R, C_v^R and C_p^R are respectively the residual enthalpy, entropy, specific heat at a constant volume and specific heat at constant pressure. C_p is the total specific heat at constant pressure and μ_{JT} is the Joule-Thomson Coefficient.

3. RESULTS AND DISCUSSION

The presented models were implemented, and the results obtained were compared with correlated data. The average absolute deviation (AAD) was calculated as follows:

$$AAD = \frac{1}{n}\sum_{i=1}^{n}\left|\frac{\phi_{cal,i} - \phi_{REF,i}}{\phi_{REF,i}}\right| \tag{19}$$

Where n is the total number of points contemplated, i refers to the point being considered , ϕ is any of the properties calculated and the subscripts *cal* and *REF* are respectively relative to the values obtained with CPA and of corelated data.

Figure 1 shows the results for specific volume for the binary system of carbon dioxide and water. In order to cover a considerable range of properties and different systems each figure in this paper will present a different system with a different property. Naturally all the properties could be calculated for each of the systems considered.

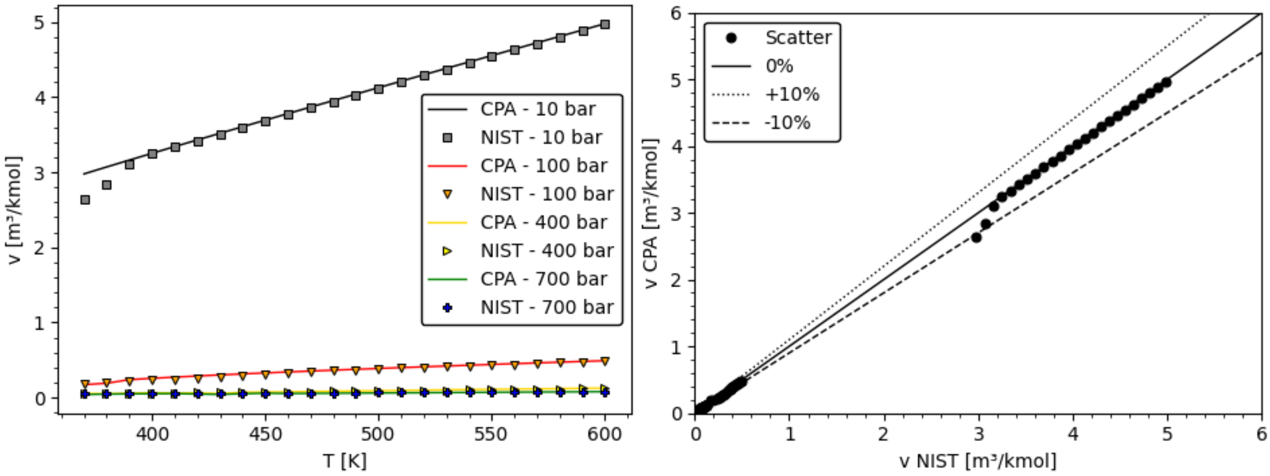

Figure 1. Specific volume (v) for CO_2 (80 %)/H_2O(20%) molar for pressures from 10 bar to 700 bar and temperatures from 320 to 600 K. Comparison with NIST (Lemmon, Huber and McLinden, 2007)

The calculated values have good correspondence with the correlated data, with the AAD being below 5%, with the majority of the punctual deviation being kept well below 10% as shown in the deviation graphic. Most of the higher deviation points are associated with condition on the vicinity of phase change. For instance, considering only the points above 480 K, away from phase boundaries, the AAD drop to 2%.

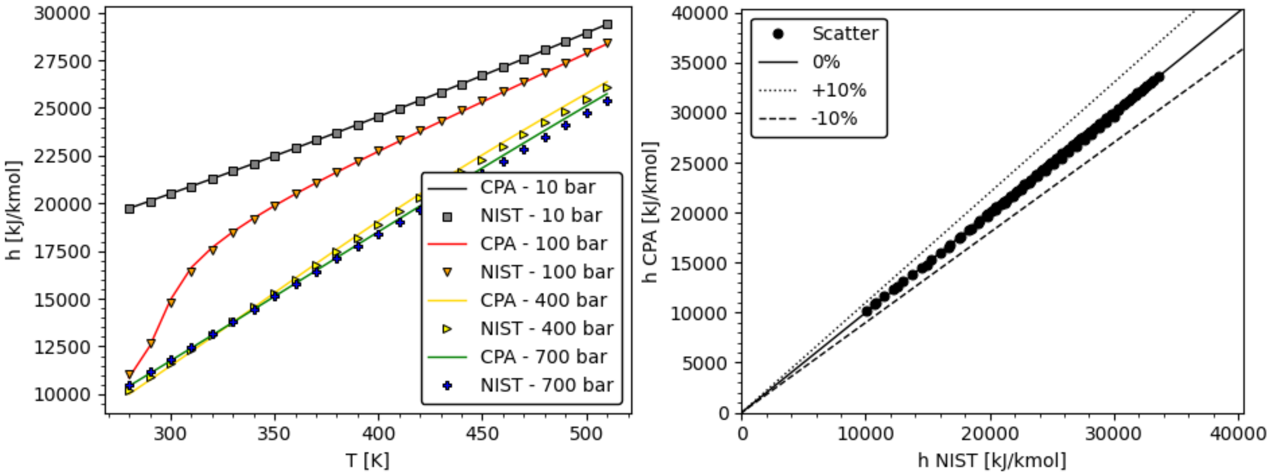

Figure 2. Enthalpy (h) for CO_2 (80 %)/CH_4(20%) molar for pressures from 10 bar to 700 bar and temperatures from 280 to 520 K. Comparison with NIST (Lemmon, Huber and McLinden, 2007)

Next it was calculated values of enthalpy for carbon dioxide plus methane, as shown in Fig (2). It can be observed that the approach used was capable of capture the physical behavior of the property, being able to produce results with low deviation for several different phases, as liquid (280 K and 100 bar), gas (280-600 K and 10 bar) and supercritical conditions (600 K and 100 – 700 bar). The average deviation found was below 1% and the maximum punctual deviation was below 2%.

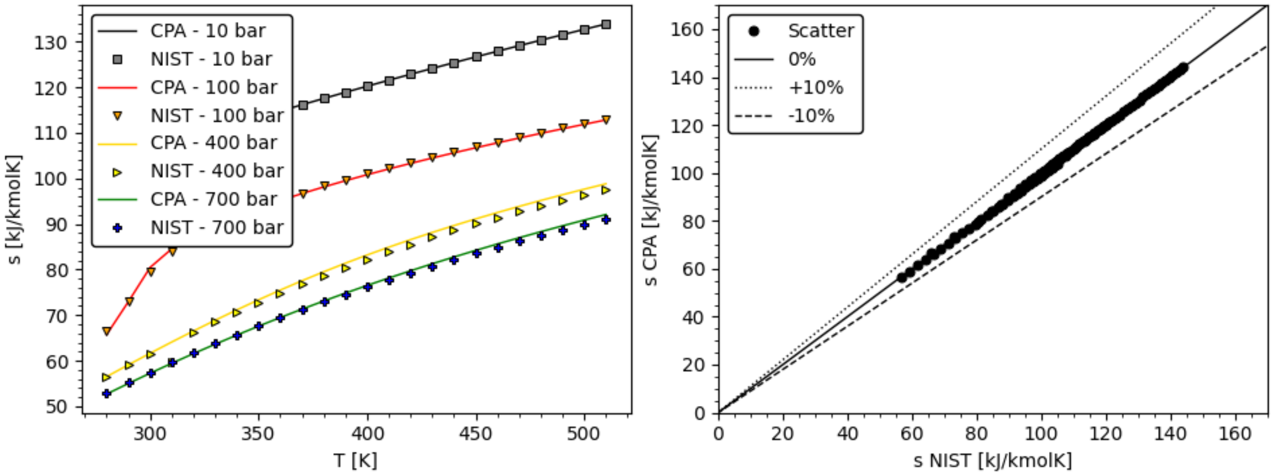

Figure 3. Entropy (s) for CO_2 (80 %)/CH_4(10%)/N_2(10%) molar for pressures from 10 bar to 700 bar and temperatures from 280 to 520 K. Comparison with NIST (Lemmon, Huber and McLinden, 2007)

Figure 3 presents the results of entropy for a ternary system containing methane and nitrogen as impurities in a mixture rich in carbon dioxide. The AAD found was 1%, with no punctual deviation than 2%. This system is of great interest because it contains two of the most common impurities in the CO_2 rich mixtures reinjected, the nitrogen, most present substance in the air, and methane, the most volatile hydrocarbon.

The specify heat at constant pressure was also calculated for a binary mixture of CO_2 and CH_4 as show in Fig (4). The AAD was below 2%, with the maximum punctual deviation being no higher than 5%. The highest deviation was observed in the vicinity of the critical point, where the property of specific heat presents sharp changes. Even with the higher deviations it is noticeable that the method was able to reproduce well the physical behavior expected.

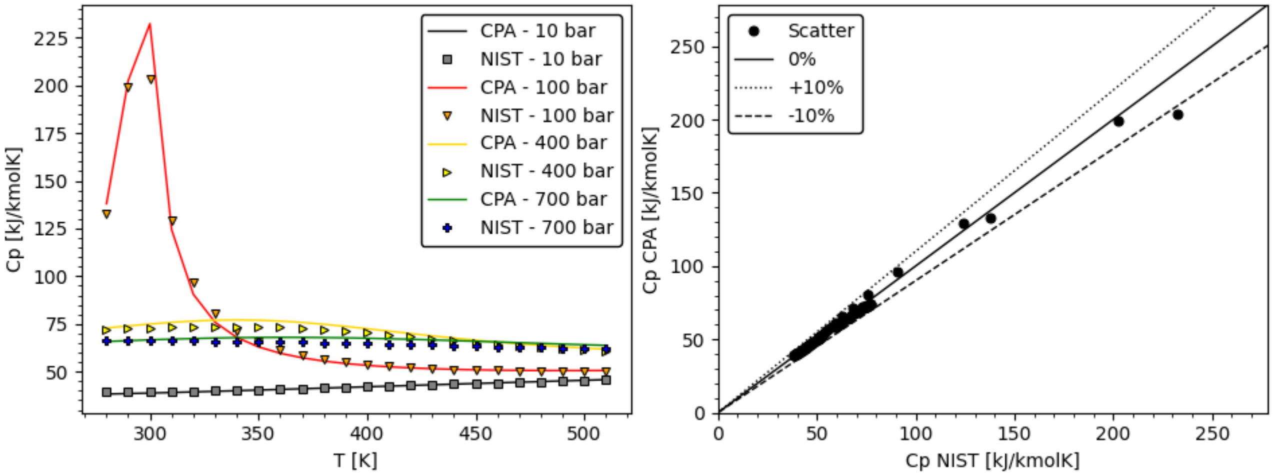

Figure 4. Specific heat at constant pressure (Cp) for CO_2 (80 %)/CH_4(20%) molar for pressures from 10 bar to 700 bar and temperatures from 280 to 520 K. Comparison with NIST (Lemmon, Huber and McLinden, 2007)

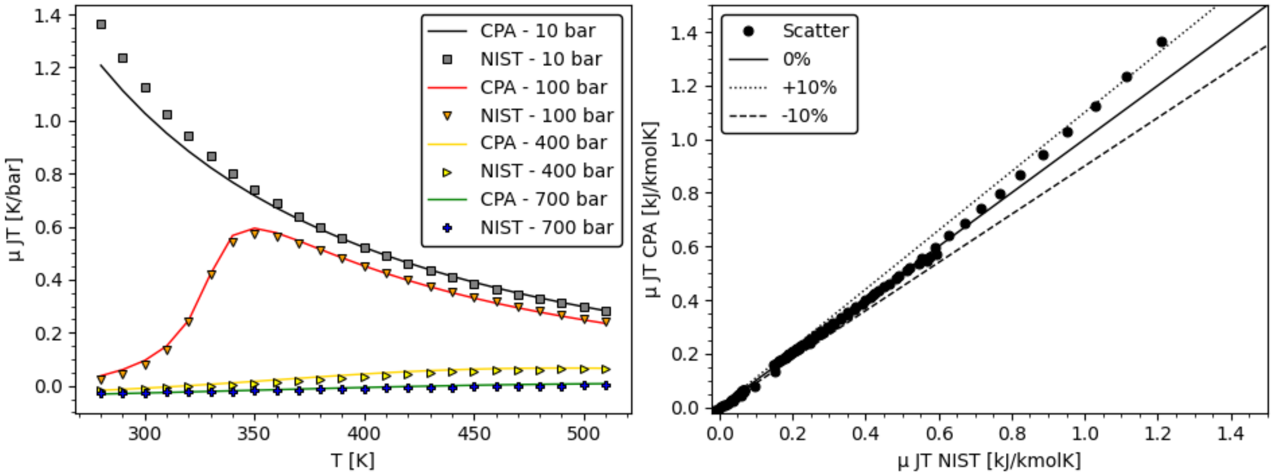

Figure 5. Joule-Thomson coefficient (μ JT) for CO_2 (80 %)/C_3H_6(20%) molar for pressures from 10 bar to 700 bar and temperatures from 280 to 520 K. Comparison with NIST (Lemmon, Huber and McLinden, 2007)

The last property considered was the Joule-Thomson Coefficient. This property is the most complex of all covered by this present paper, applying not only other properties calculated but also derivatives of them. Nevertheless, the results found were satisfactory showing that the approach applied was capable of reproducing accurately the expected behavior of the Joule-Thomson coefficient for all isobaric curves tested. The AAD for the isobaric curves of 10 bar and 100 bar were 2% and 6% respectively.

4. CONCLUSION

It was presented an approach for the determination of the specific volume, enthalpy, entropy, specific heat and Joule-Thomson coefficient. The proposed method applies the CPA EoS plus departure functions, and it was it was tested for mixtures rich in carom dioxide plus contaminants such as water, nitrogen and hydrocarbons. The range of conditions of temperature and pressure were compatible with what is expected in the activities of reinjection of CO_2.

The results were then compared with correlated data. It was shown that the deviations found were generally well below 10%, with exception of some extreme conditions. This shows that a CPA cubic equation of state can be a viable alternative for predicting the main properties of state for CO_2 rich mixtures.

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