

PREDICTION OF THERMODYNAMIC PROPERTIES OF PETROLEUM AND REFINERY GASES USING PC-SAFT+FVT MODEL

Luu Tra My¹, Nguyen Huynh Dong¹, Nguyen Huynh Duong²

¹Petrovietnam Manpower Training College (PVMTC)

²Petrovietnam Gas Joint Stock Corporation (PV GAS)

Email: dongnh@pvmtc.com.vn

Summary

The PC-SAFT equation of state (EoS) combined with the free-volume theory (FVT) recently proposed (DOI: 10.1016/j.fluid.2019.112280) is extended in this work to simultaneously predict viscosity and some second-order derivative properties such as sound velocity and isobaric heat capacity of some petroleum and refinery gases. The PC-SAFT pure component parameters are obtained by providing the optimal description of its vapour pressure and saturated liquid density data. New FVT parameters were derived for various petroleum and refinery gases and were validated with the National Institute of Standards and Technology's data over a wide range of temperature and pressure (up to 2,000 bars). The model is simple to incorporate into the design and simulation package such as Aspen Plus or Prosim, with average absolute deviation obtained on viscosity within the experimental uncertainty (< 3%), which is appropriate for most industrial applications.

Key words: Viscosities, PC-SAFT, prediction, thermodynamic, petroleum gases.

1. Introduction

The importance of gases in oil recovery operations is increasing, as evidenced in the successful use of gases such as carbon dioxide, nitrogen and their mixtures as injection gases in enhanced oil recovery. The simulation and modelling using the simulation package allow to reduce capital, time and cost related to the operation of oil and gas processing units and pipeline transportation. In this, the viscosity model is an important component of the package, ranging from the simulation of gas production at reservoir condition to the design and operation of pipeline transportation or petrochemical plant. Although the experimental data are available for numerous petroleum gases, there is still a need for a generalised estimator that is able to predict the thermodynamic properties of molecules over a wide range of thermodynamic conditions, particularly at extreme temperature and pressure condition.

Simultaneous prediction of transport properties and fluid phase equilibria using equation of state is

still an important subject in the oil and gas industry. So, the development of a thermodynamic model with good accuracy in predicting the phase equilibria and thermodynamic properties of fluids is a great importance. In this paper, the applicability of the PC-SAFT+FVT model is assessed on petroleum and refinery gases.

2. PC-SAFT + FVT model

In previous works, the PC-SAFT + FVT model has been proposed based on the assumption that the viscosity of real fluids could be directly related to PC-SAFT molecular parameters [1]. Our model has been successfully applied to calculate the viscosity of several kinds of molecules such as alkane, cycloalkane, alcohols, aromatics and their mixtures [1, 2]. In this work, we apply, for the first time, the PC-SAFT+FVT model to the calculation of the thermodynamic second-order derivative properties and the viscosity of several gases.

2.1. PC-SAFT EoS

The original PC-SAFT EoS is expressed as a sum of different residual Helmholtz terms [3]:

$$a^{\text{res}} = a^{\text{hc}} + a^{\text{disp}} \quad (1)$$

For all gases studied in this work, they are considered as non-associative, non-polar molecules. PC-SAFT EoS requires three parameters to describe these components (dispersive energy - ϵ/k , segment diameter - σ and segment number - m). The readers are referred directly to the original papers for more details about the PC-SAFT EoS [3]. All expressions used to calculate different thermodynamic properties such as heat capacity or speed of sound are explained in the references [4 - 6].

2.2. Free-volume theory

The fluids' viscosity by FVT consists of two terms [1]:

$$\eta = \eta_0 + \Delta\eta \tag{2}$$

The first term called dilute gas viscosity (η_0) is expressed as [1]:

$$\eta_0 = 26.69 \frac{\sqrt{M T}}{\sigma^2 \Omega^*} \frac{F_c}{10^6 m^{1.5}} \tag{3}$$

In which T , M , and η_0 are temperature (K), mass molecular (g/mol) and gas viscosity, respectively; σ and m are PC-SAFT EoS hard-sphere diameter (Å) and segment number. The reduced collision integral (Ω^*) is calculated using Equation (4) [7].

$$\Omega^* = \frac{1.16145}{T^{*0.14874}} + \frac{0.52487}{\exp(0.7732T^*)} + \frac{2.16178}{\exp(2.43787T^*)} \tag{4}$$

$$-6.435 * 10^{-4} T^{*0.14874} \sin[18.0323T^{*-0.7683} - 7.27371]$$

The dimensionless temperature (T^*) is a function of temperature and PC-SAFT dispersive energy of pure compound, small gases:

$$T^* = \frac{T}{\epsilon/k}$$

The other contribution of viscosity in Equation (2) is the residual viscosity ($\Delta\eta$), that could be estimated based

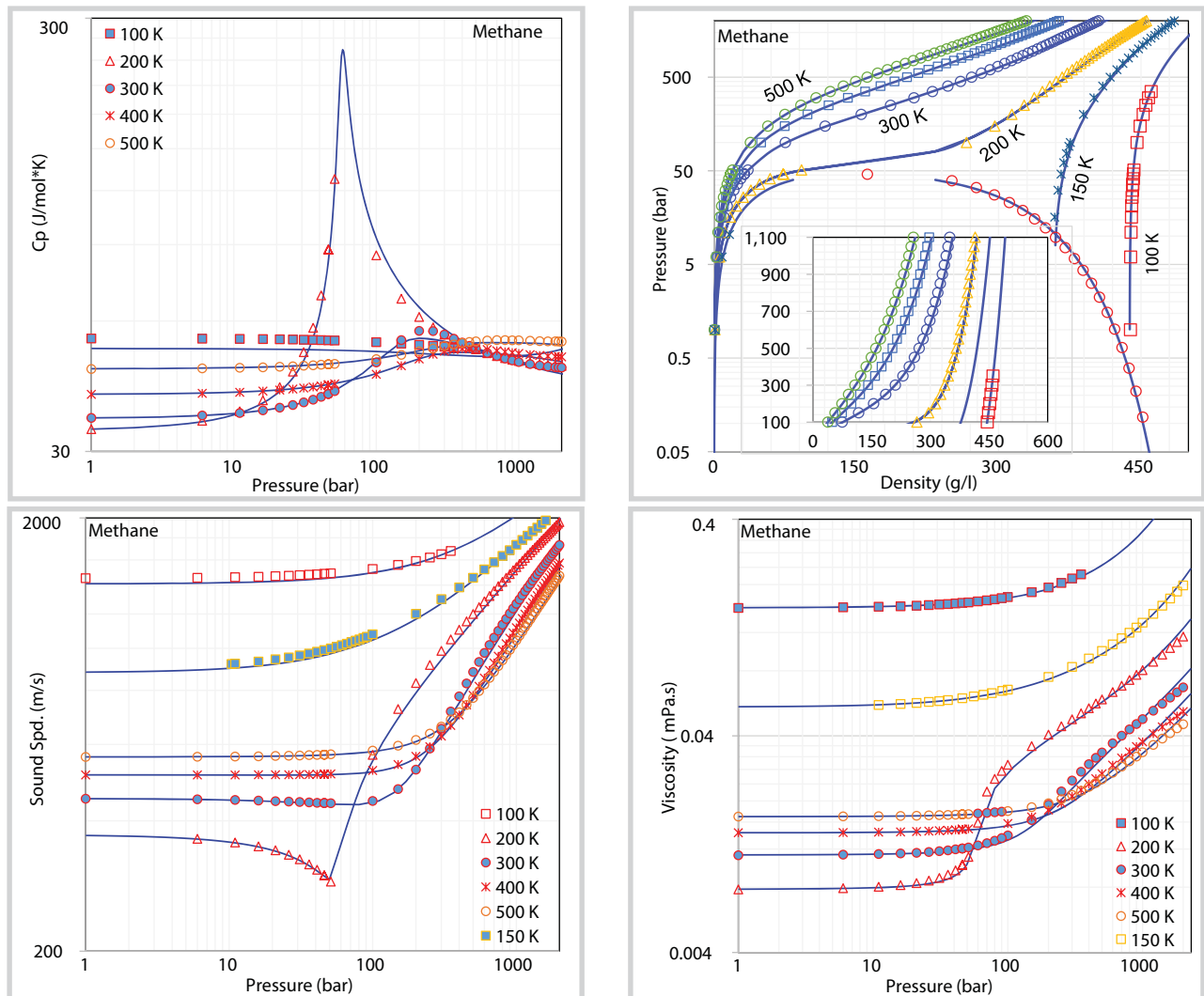


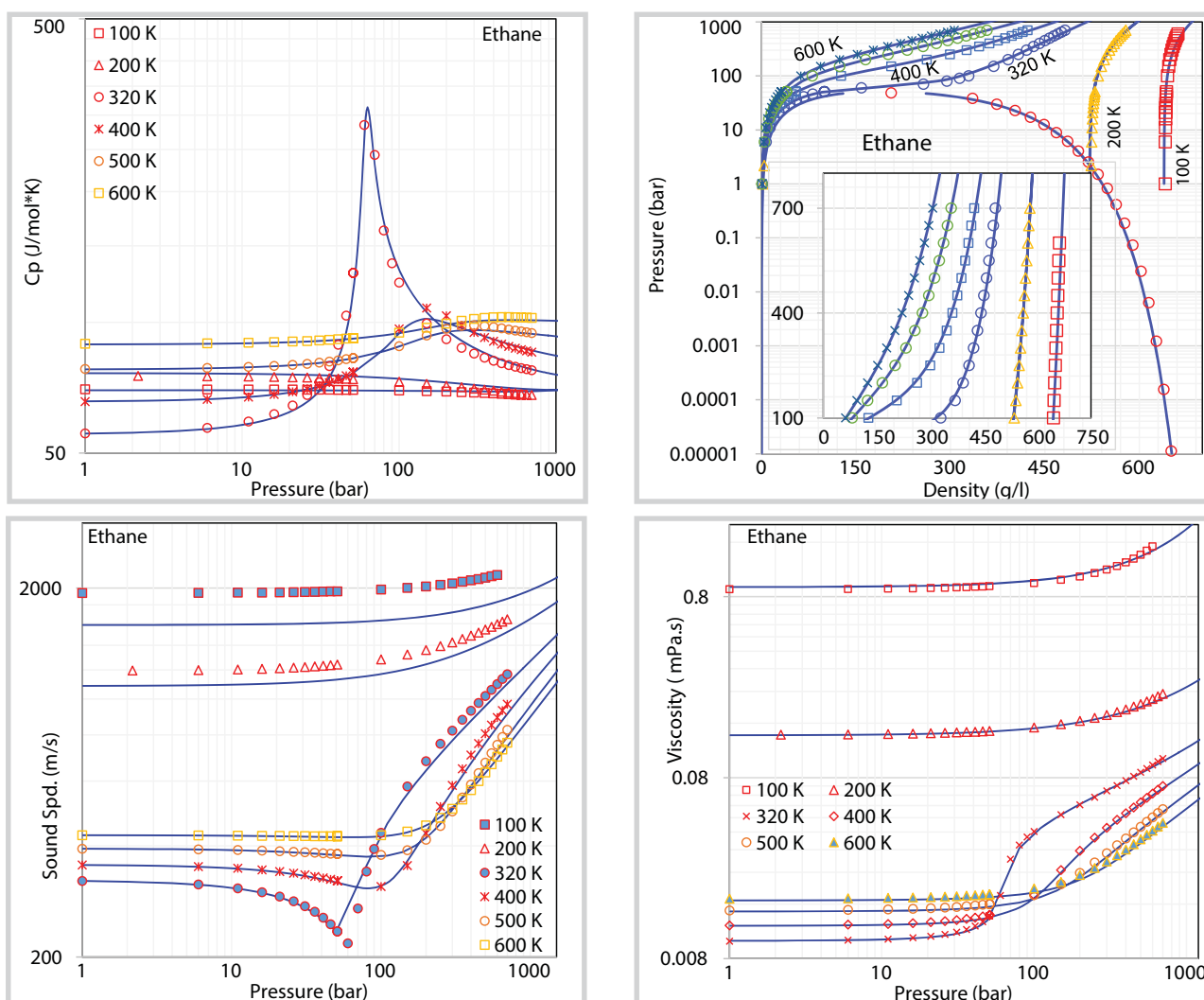
Figure 1. Predicted and experimental (NIST Chemistry Web Book) isobaric heat capacity, liquid density, viscosity and speed of sound of methane.

Table 1. PC-SAFT+FVT model parameters for gases [9, 10]

Compound	ϵ/k (K)	σ (Å)	m	$L \times 10^3$ (Å)	$a \times 10^{-3}$ (J m ³ /mole kg)	F_p	$F_c \times 10^{-2}$
Iso-butane	205.942	3.6584	2.4587	3.4260	3.9298	1.0	2.2908
Oxygen	113.642	3.1759	1.1481	2.5913	0.5549	1.35	1.0599
Carbon monoxide	89.394	3.1964	1.3699	5.5051	0.5709	0.15	1.2044
Carbon dioxide	151.734	2.5608	2.5807	1.9059	1.6735	2.8	1.6207
Nitrogen	89.468	3.2945	1.2376	1.6560	0.9291	1.85	1.1037
Methane	150.037	3.7042	1.0003	2.1652	2.3798	1.0	0.9832
Ethane	189.001	3.5098	1.6364	3.7890	2.4022	1.35	1.2336

Table 2. The average absolute deviation (AAD) for the PC-SAFT+FVT for all of the investigated molecules. Experimental data are taken from DIPPR [8]

Compound	Vapour pressure		Liquid density		Liquid viscosity		Vapour viscosity	
	T (K)	AAD (%)	T (K)	AAD (%)	T (K)	AAD (%)	T (K)	AAD (%)
Oxygen	54 - 154	0.67	54 - 154	0.92	54 - 132	1.83	54 - 600	0.81
Carbon monoxide	68 - 132	0.38	68 - 132	1.48	68 - 124	3.83	68 - 600	1.17
Carbon dioxide	216 - 304	0.28	216 - 304	1.38	200 - 304	1.08	270 - 610	1.83
Nitrogen	63 - 126	0.24	63 - 126	1.41	64 - 122	2.60	64 - 600	0.56
Methane	90 - 190	0.51	90 - 190	1.10	84 - 186	0.40	84 - 600	0.31
Ethane	90 - 305	0.67	90 - 305	1.31	90 - 302	1.69	90 - 600	1.29
Iso-butane	123 - 407	3.28	123 - 407	2.22	114 - 310	1.95	150 - 600	1.95


Figure 2. Predicted and experimental (NIST Chemistry Web Book) isobaric heat capacity, liquid density, viscosity and speed of sound of ethane.

on the expression previously suggested [1]:

$$\eta = \eta_0 + 10^{-7} \rho L E \sqrt{\frac{1000}{3 m R T}} \exp \left[2.10^{-5} \left(\frac{E}{R T} \right)^{1.5} \right] \quad (5)$$

$$\text{and } E = \alpha \rho + F_p \frac{P}{\rho} 10^5$$

Where the viscosity is given in mPas; R is universal gas constant (8.314 J/mol.K) and P is pressure (in bar). The liquid density (ρ , in kg/m³) is the only property yielded by the PC-SAFT. L is the length parameter (in Å) which is related to the molecular size, α is the barrier energy required for self-diffusion (in J m³/(mol.Kg)), and F_p is the free-volume overlap. These last three parameters are

characteristic parameters of fluid according to FVT theory. The FVT parameter triplet set and the F_c can be obtained by regressing to the experimental viscosity data.

3. PC-SAFT+FVT parameters regression

Six petroleum and refinery gases and oxygen have been studied. These gases have been selected to test the model due to the availability of experimental data. The regression of PC-SAFT+FVT model parameters has been carried out in a sequential manner, with alternate optimisation of the PC-SAFT EoS parameters and then the correction factor (F_c) and the FVT triplet set in Equation (5)

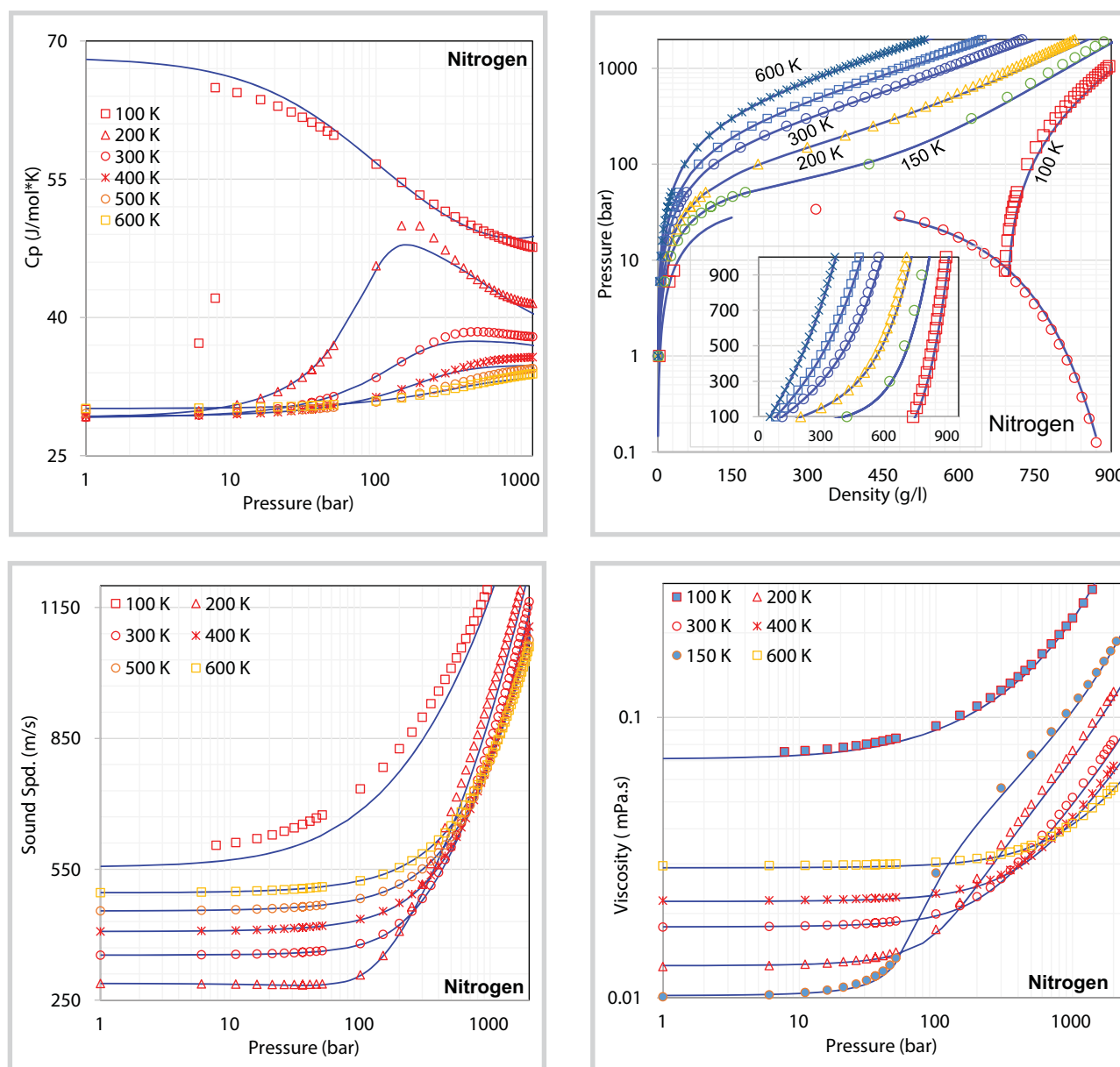


Figure 3. Predicted and experimental (NIST Chemistry Web Book) isobaric heat capacity, liquid density, viscosity and speed of sound of nitrogen.

were next determined by minimising a quadratic residual defined by relative viscosities.

Step 1: The PC-SAFT EoS parameters of petroleum and refinery gases were determined by simultaneously fitting on its vapour pressure and saturated liquid density. The regression function that was used is written as:

$$F_{obj} = \frac{1}{N_{p^{sat}}} \sum_1^{N_{p^{sat}}} \left(\frac{P_{cal}^{sat} - P_{exp}^{sat}}{P_{exp}^{sat}} \right)^2 + \frac{1}{N_{\rho^{liq}}} \sum_1^{N_{\rho^{liq}}} \left(\frac{\rho_{cal}^{liq} - \rho_{exp}^{liq}}{\rho_{exp}^{liq}} \right)^2 \quad (6)$$

Where $N_{p^{sat}}$ and $N_{\rho^{liq}}$ are the number of the experimental vapour pressures and saturated liquid density data, respectively. The choice of data for each

component is dictated by the availability of experimental data from the Design Institute for Physical Property Data (DIPPR) [8].

Step 2: Having three PC-SAFT parameters, the correction factor (F_η) of gases is fitted using their dilute gas viscosity data. Three adjustable parameters (L, α, F_p) in Equation (5) were obtained by fitting the model to the saturated liquid viscosity.

The PC-SAFT+FVT model parameters for different gases considered in this work are reported in Table 1. Table 2 represents the experimental data sources and deviations obtained with PC-SAFT+FVT model for pure gases. For all

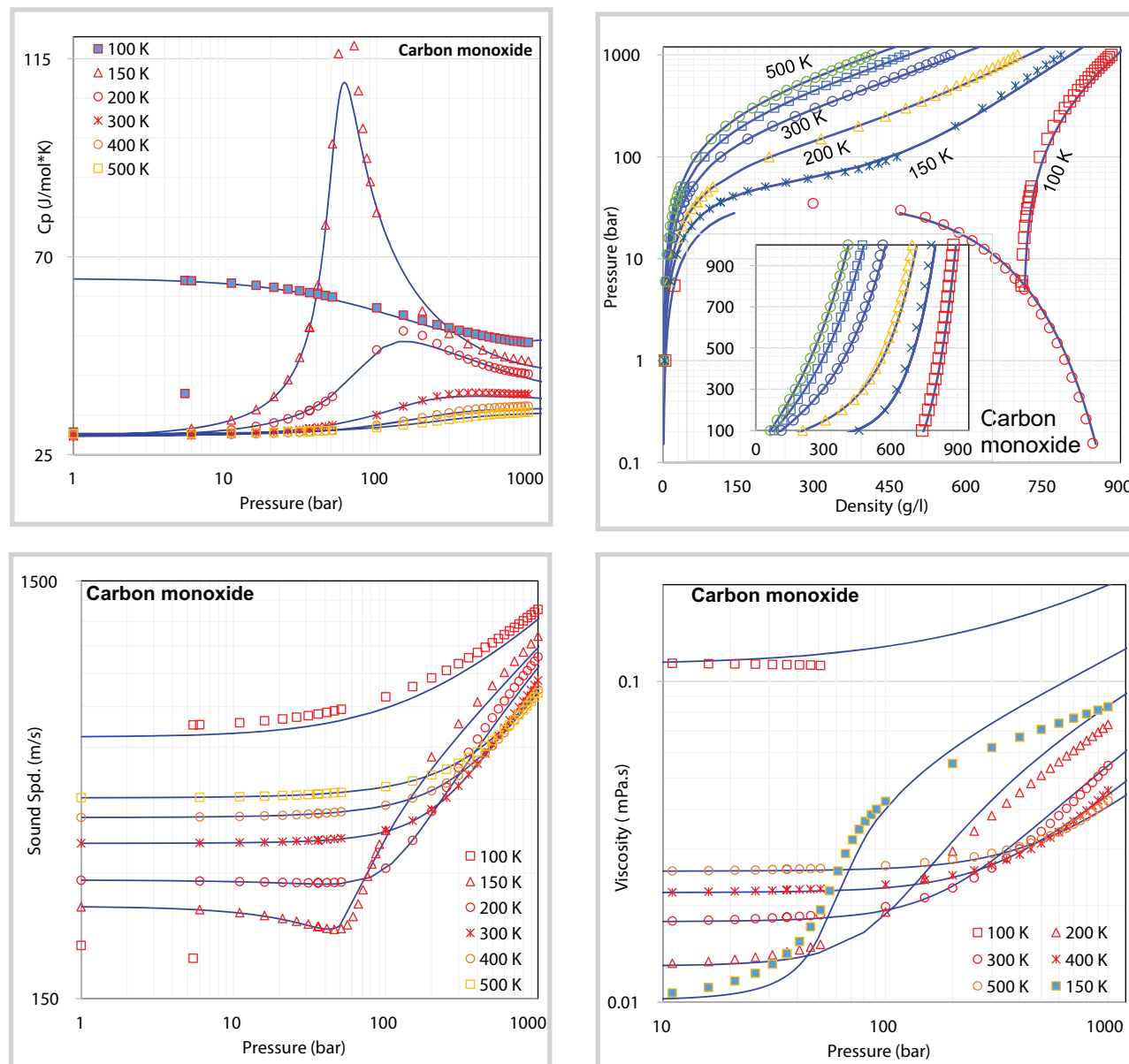


Figure 4. Predicted and experimental (NIST Chemistry Web Book) isobaric heat capacity, liquid density, viscosity and speed of sound of carbon monoxide.

cases, the average absolute deviation obtained on vapour pressure, liquid density and saturated viscosities is within the experimental accuracy (lower than 2%) [2].

The deviation is defined as:

$$AAD(\%) = 100 \cdot \sum_{data} \frac{|\eta_{exp} - \eta_{cal}|}{\eta_{exp}} \quad (7)$$

4. Results and discussion

The liquid density, isobaric heat capacity, speed of sound and viscosity of seven gases were predicted in the temperature range of 100K to 600K and pressure up to 2,000 bars. This extrapolation test seems to be more

stringent than their correlation accuracy. This prediction also allows to validate the prediction potential of the model over a wide range of thermodynamic conditions.

Figures 1 to 7 show the comparison between the predicted values obtained with the current model and the experimental data of several petroleum gases in both sub- and super critical regions. The experimental data are taken from the NIST chemistry web book (<http://webbook.nist.gov/chemistry/fluid>). An excellent match between the predicted and experimental liquid density and viscosity was obtained for all considered gases. Considering the results of these figures, it is evident that the PC-SAFT+FVT model provides a very good result for heat capacity. The

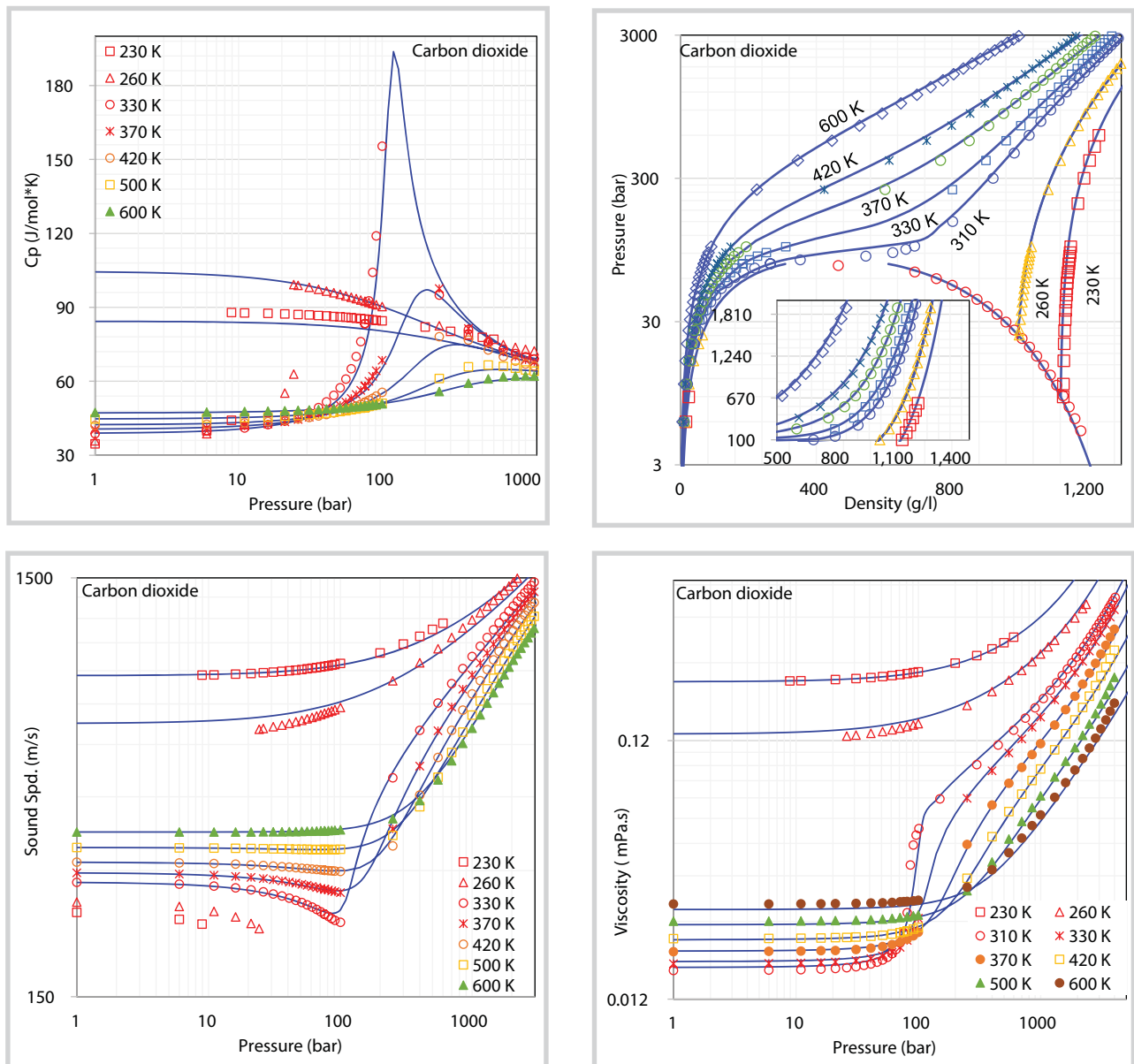


Figure 5. Predicted and experimental (NIST Chemistry Web Book) isobaric heat capacity, liquid density, viscosity and speed of sound of carbon dioxide.

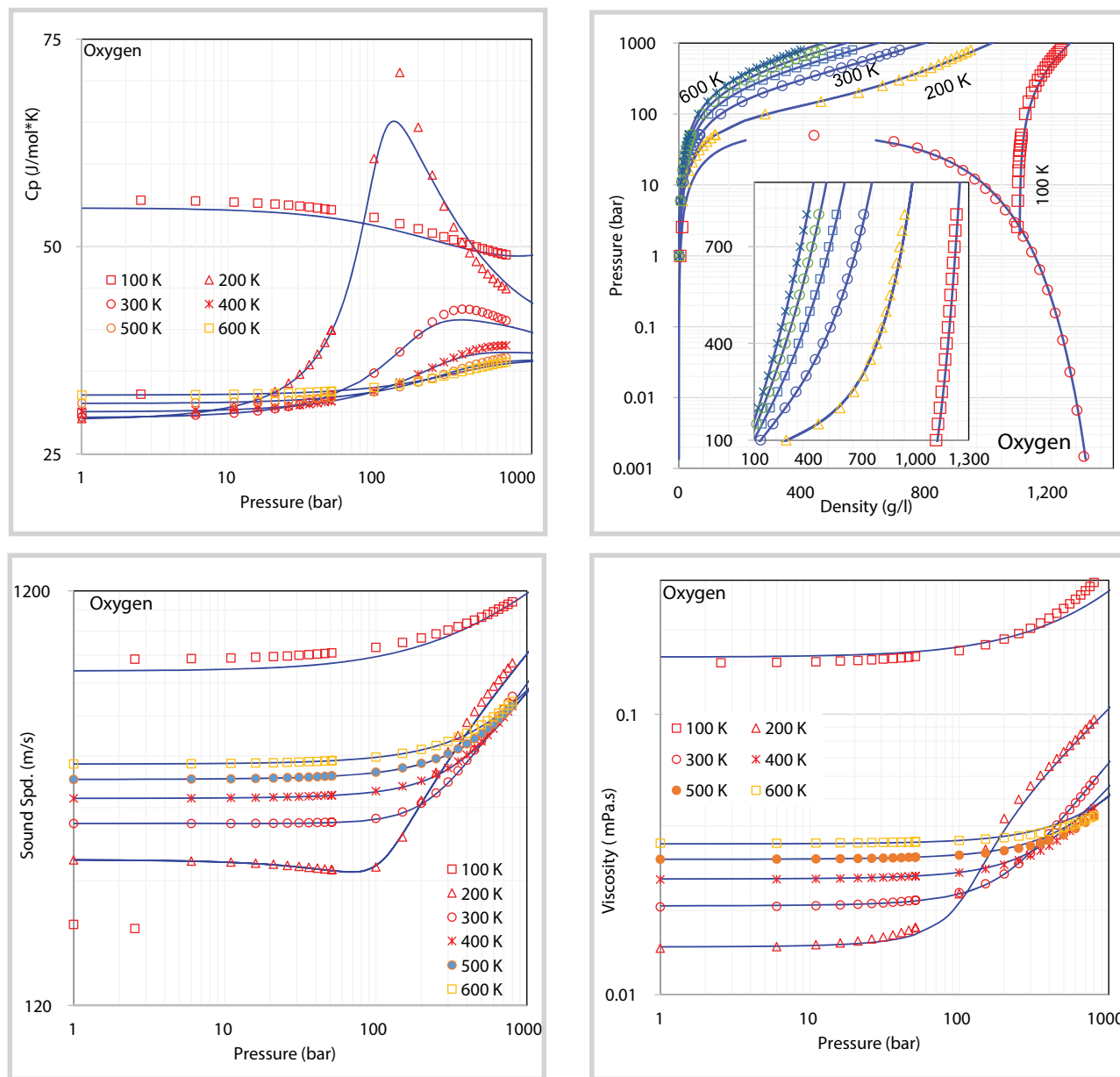


Figure 6. Predicted and experimental (NIST Chemistry Web Book) isobaric heat capacity, liquid density, viscosity and speed of sound of oxygen.

average absolute deviation results from experimental data is around 1 - 3% for most of cases, except for iso-butane, at temperature lower than 200K, the predicted values deviate largely from the measured data. In fact, the speed of sound is generally represented as a severe consistency test for any EoS, since it involves the temperature and density partial derivatives of pressure, and PC-SAFT is not able to describe with great accuracy the $p(\rho, T)$ [4 - 6]. The model was also not able to reproduce the transition regions, e.g. for iso-butane, the model could not match the 350K isotherm data ranging from 1 bar to 10 bars, for both speed of sound and viscosity [11].

5. Conclusion

In this work, the PC-SAFT+FVT model has been applied to some petroleum and refinery gases. The pure component parameters for several gases have been reported. Single phase liquid density, isobaric heat capacity, sound velocity and viscosity of these molecules have been predicted and compared with experimental data. Results have indicated that with the exception of the speed of sound at condition lower than 200K, PC-SAFT+FVT accurately predicts the thermodynamic properties of petroleum and refinery gases. PC-SAFT is not adequate for predicting the isobaric heat capacity

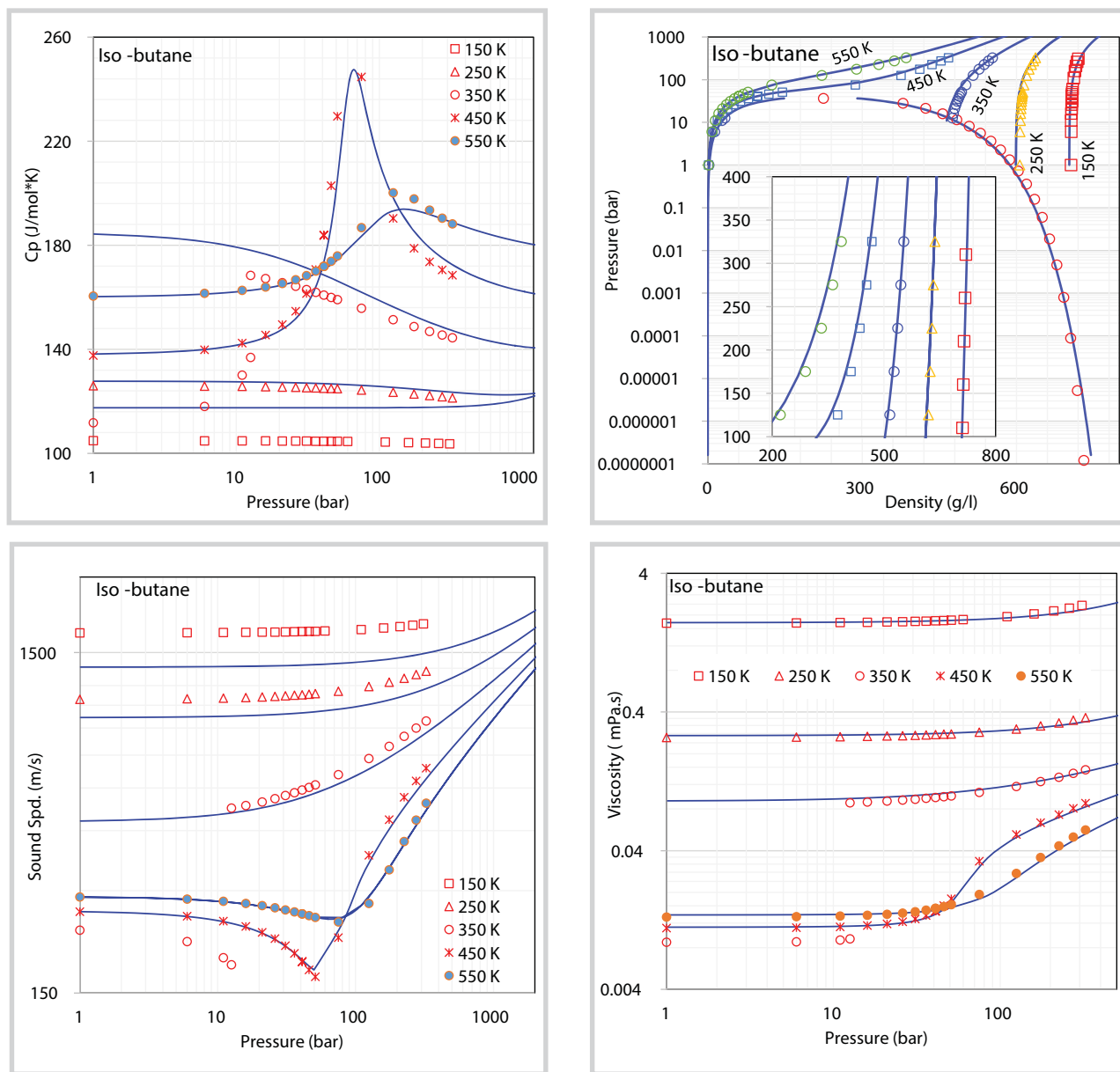


Figure 7. Predicted and experimental (NIST Chemistry Web Book) isobaric heat capacity, liquid density, viscosity and speed of sound of iso-butane.

of iso-butane at temperature lower than 450K. These deviations were already observed in the prediction of other similar pure fluids such as alkanes or non-polar molecules [6, 12].

For conclusion, the PC-SAFT+FVT model could be used as a robust estimator for the thermodynamic properties of petroleum gases with good accuracy, particularly in the temperature and pressure conditions of interest in the oil and gas industry. The model is simple to incorporate into the design and simulation package such as Aspen Plus or Prosim, with the average absolute deviation obtained by the model being within the experimental incertitude.

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