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Viscosity measurements of (CH_4 + C_3H_8 + CO_2) mixtures at temperatures between (203 and 420) K and pressures between (3 and 31) MPa

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ABSTRACT

In this work, viscosity measurements of the ternary mixture [$0.6511CH_4 + 0.0808C_3H_8 + 0.2681CO_2$] were made over the temperature range (203–420) K and at pressures up to 31 MPa, with a combined overall standard uncertainty of 2.5%. The presence of CO_2 or propane in the ternary mixture was found to always increase the viscosity relative to the constituent binary mixtures with larger differences observed at the highest density conditions: adding 26.8% mole fraction of CO_2 to the binary mixture [$xCH_4 + (1-x)C_3H_8$] with $x = 0.8888$, increased the viscosity by up to 45%. Similarly, adding 8.1% mole fraction of propane to the binary mixture [$xCH_4 + (1-x)CO_2$] with $x = 0.7084$, increased the viscosity by up to 23%; in this case, while the effect was apparent at lower temperatures, it was negligible at 370 K and above. The ternary mixture data were compared with the predictions of five models: corresponding states based approaches (ECS, SuperTRAPP and PFCT), the LBC model used widely by petroleum engineers, and a model (LJ) based on molecular dynamics simulations of Lennard Jones fluids. The relative deviations of the measured viscosities from those calculated by the five models exhibited a similar, systematic dependence on density, with stronger and larger systematic relative deviations observed at the lowest temperatures. The average absolute deviations from the measured viscosities were 2.5%, 6.4%, 8.0%, 4.2% and 3.9% for the ECS, ST, PFCT, LBC and LJ models respectively, with the ECS model providing a better representation of the data over the entire range. The present study reveals how well various engineering models can describe the viscosity of a multi-component mixture under supercritical conditions, which are of increasing interest in the energy industrial sector.

1. Introduction

Carbon dioxide, methane and propane are key constituents of many important and/or emerging industrial processes such as carbon sequestration, CO_2-enhanced oil recovery (CO_2-EOR) and the production of liquefied natural gas (LNG). Each stage of these processes is designed using predictions of the mixture's thermodynamic and transport properties over wide ranges of pressure, temperature and composition conditions. However, the extent to which engineering margins are used in such designs is mainly influenced by the accuracy of the property predictions (such as viscosity) used in the process simulation [1–3]. The accuracy of the models used for predicting the fluid properties are in turn dependent on the extent and uncertainty of experimental data used to develop and validate the model. To our knowledge, viscosity data for ternary or multi-component mixtures containing methane, propane and carbon dioxide at conditions relevant to oil and gas processing are extremely limited in the open literature. Most of the mixture data available in the literature consider binary systems [4–19]. While binary data (and pure component data) are often needed for tuning the parameters of predictive models, high-quality viscosity data for multi-component mixtures are needed to validate the predictions of such models.

The available literature viscosity data for the two binary subsystems (methane-propane and methane-CO_2) as well as those available for natural gas mixtures are summarized in Table 1.

While there exists good data sets for the binaries [$CH_4 + C_3H_8$] and [$CH_4 + CO_2$], the data available for [$C_3H_8 + CO_2$] are limited to a pressure $p = 0.1$ MPa only [17–19]. Those data were obtained for temperatures T between (298 and 550) K and x in the range (0–1), corresponding to densities in the range (0.96–1.96) kg·m^{-3}.

Stanwix et al. [7] and Czubinski et al. [8], presented detailed comparisons of four predictive viscosity models relative to their

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Table 1
Literature viscosity data for the binaries and natural gas mixtures.*

Author	Mixture	x_1	T/K	P/MPa	ρ/kg·m^3	Method
Locke et al. [6]	$x_1CH_4 + x_2C_3H_8$	0.945	280, 298	0.6 to 6.9	4.7 to 64	VWV
Stanwix et al. [7]	$x_1CH_4 + x_2C_3H_8$	0.949	200 to 423	10 to 31	120 to 360	VWV
Czubinski et al. [8]	$x_1CH_4 + x_2C_3H_8$	0.889	200 to 420	2 to 32	14 to 382	VWV
Giddings et al. [9]	$x_1CH_4 + x_2C_3H_8$	0.22 to 0.79	311 to 411	0.1 to 55.1	0.6 to 506	CV
Huang et al. [10]	$x_1CH_4 + x_2C_3H_8$	0.22 to 0.75	153 to 311	3.4 to 34	34 to 645	FC
Bicher and Katz [11]	$x_1CH_4 + x_2C_3H_8$	0.2 to 0.8	298 to 498	0.1 to 34.4	0.5 to 513	RB
Locke et al. [6]	$x_1CH_4 + x_2CO_2$	0.570	280 to 328	1.5 to 36.5	16 to 102	VWV
Stanwix et al. [5]	$x_1CH_4 + x_2CO_2$	0.483	229 to 348	1 to 32	20 to 600	VWV
Kestin et al. [13,14]	$x_1CH_4 + x_2CO_2$	0.144 to 0.674	293, 303	0.1 to 2.6	1 to 50	OD
Dewitt and Thodos [15]	$x_1CH_4 + x_2CO_2$	0.243 to 0.755	323 to 473	3.4 to 68	1 to 792	CV
Davani et al. [16]	$x_1CH_4 + x_2CO_2$	0.9	310 to 455	34 to 172	160 to 457	OP
Jackson [12]	$x_1CH_4 + x_2CO_2$	0 to 1	298	0.1	0.65 to 1.8	CV
Atilhan et al. [20]	Natural gas	0.850, 0.903	250 to 450	10 to 65	50 to 450	OP
Assael et al. [21]	Natural gas	0.848	240 to 455	0.1 to 15	1.3 to 135	VWV
Langelandsvik et al. [22]	Natural gas	0.902, 0.800, 0.922	263 to 303	5.0 to 25	37 to 326	VWV

* VWV: vibrating wire viscometer; CV: capillary viscometer; FC: falling cylinder; RB: rolling ball; OD; oscillating disk; OP; oscillating piston.

experimental data for [xCH$_4$ + $(1-x)$C$_3$H$_8$] as well as the data published by Giddings et al. [9], Huang et al. [10] and Bicher and Katz [11]. Two of these models, the ECS [23] and SUPERTRAPP (ST) [24] models, are based on the corresponding states theory [23] while the third model [25,26], LJ, is a predictive model derived from molecular simulations combined with a corresponding states scheme. The VW model [27–30], is a semi-theoretical approach based on hard-sphere molecules in which the viscosity of a mixture is related to the viscosity of each individual component at the temperature and molar volume of interest. The comparisons showed a systematic deviation of about −5% in the predictions of the ECS model around $\rho \approx 160$ kg·m^{-3}, which is near the critical density of pure methane. Overall, the VW model had the closest agreement for the entire data set included in their comparison. Locke et al. [5] compared the data reported for [xCH$_4$ + $(1-x)$CO$_2$] and those available in the literature with the predictions made by ECS [23] and SUPERTRAPP (ST) [24] models, and the LJ model [25,26]. In their work, they found that the measured viscosities deviated systematically from those predicted by both the ECS and SUPERTRAPP models with deviations that increased with higher density and/or lower temperatures. In contrast, the LJ model reproduced the density and temperature dependence of the measured viscosities well, with relative deviations of less than 4.2%.

In their study of two synthetic methane-rich natural gas mixtures, Atilhan et al. [20] compared their viscosity data with the predictions made by SUPERTRAPP (ST) [24], the CLS (Chung, Lee, and Starling) model developed by Chung et al. [31,32], the LBC (Lohrenz, Bray, and Clark) model developed by Lohrenz et al. [33] and the PFTC (Pedersen, Fredenslund, Thomassen, and Christensen) model developed by Pedersen et al. [34,35]. The CLS model is used for predictions of viscosity, critical temperature, and critical pressure for homologous hydrocarbon series via the carbon number using an empirical equation, while the LBC model is a 16th degree polynomial in the reduced density. The PFTC model is based on the principle of corresponding states with methane and decane as reference components. In their comparison, they reported that the PFTC model was most consistent with the experimental data, with an AAD of 3%. Subsequently, Assael et al. [21] compared the viscosity data for the natural gas mixture measured by Atilhan et al. [20] with the predictions of the VW model [27–30]. The VW method was found to perform very well and was able to reproduce all the available experimental data with a maximum deviation of 3.8%.

Langelandsvik et al. [22] compared their viscosity data for natural gas mixtures with a variety of models including the semi-empirical Lee–Gonzalez–Eakin (LGE) scheme, [36] which is based on a database of more than 3000 viscosity measurements of gaseous hydrocarbon mixtures. Comparisons were also made with the SUPERTRAPP (ST) model [23] and the VW models [27–30]. Both the LGE and ST models were found to agree reasonably well with the experimental data for all natural gas mixtures with 2% AAD. A comprehensive review on the available experimental and models for natural gas mixtures was presented by Vesovic [37]. In that work, the predictions with four different models (LBC [33], PFTC [34,35], SUPERTRAPP [24] and VW [38,39]) were compared with the available experimental data for natural gas mixtures that covered the temperature range (240–444) K and pressures up to 55 MPa.

To our knowledge, no viscosity data have been reported for the ternary mixture [CH$_4$ + C$_3$H$_8$ + CO$_2$]. In the present work, and to test further the performance of the widely used viscosity models against multicomponent mixture data, viscosity measurements for the ternary mixture [0.6511CH$_4$ + 0.0808C$_3$H$_8$ + 0.2681CO$_2$] are reported. Fig. 1 shows the location in the (ρ,p) and (p, T) plane of the measurements conducted in this work for the ternary mixture, relative to its phase envelope, which was calculated using the GERG-2008 EOS [40]. The measurements cover the ranges (204–420) K and (3–31) MPa, with a total of 75 viscosity data points being acquired from (12 to 84) μPa·s at densities from (27 to 563) kg·m^{-3}. The measurements were conducted in the dense phase and the vapor phase regions over a wide range of temperatures spanning below and above the mixture cricondentherm temperature, T = 257.7 K. The critical pressure, temperature and density of this mixture are predicted by the GERG 2008 EOS to be 8.01 MPa, 244.6 K and 285.8 kg·m^{-3}, respectively.

In the present work, the predictions of five models were compared with the experimental data. The models chosen are used widely in the natural gas industry. The first two models, the ECS [23] and SUPERTRAPP (ST) [24] are based on the corresponding states theory [23], and are implemented in the software packages REFPROP 9.1 [41] and Multiflash 4.4 [42,43], respectively. The basis of those models is the principle of corresponding-states, where the properties of a pure fluid or mixture are inferred from those of a reference fluid for which the properties are well known over wide range of conditions. This is then transferred to mixtures by means of combining and mixing rules that usually require the knowledge of four binary interaction parameters involved in the scaling shape functions (f and h), as well as the Lennard-Jones (LJ) collision diameter (σ) and potential energy (ε) parameters. In the older SUPERTRAPP model, the shape factors are functions of temperature only while they are functions of both temperature and density in the ECS approach implemented in REFPROP 9.1.The third model, PFTC [34,35], is also based on the corresponding states theory [23], and implemented in the Multiflash 4.4 [42,43] software package. In this approach, methane and decane are used as reference fluids, and the viscosity of a given component or mixture is determined from the reduced viscosities of the reference components using reduced pressures and the molecular weight as an interpolation parameter. The fourth is