



High-temperature, high-pressure viscosity of *n*-octane and isooctane



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ABSTRACT

Experimental viscosity data are reported for *n*-octane and isooctane (2,2,4-trimethylpentane) at pressures between 4 and 242 MPa and temperatures between 303 and 523 K. These extreme conditions are representative of those encountered in ultra-deep petroleum formations beneath the deepwaters of the Gulf of Mexico. The measurements are performed using a windowed, variable-volume, rolling-ball viscometer. A comparison of reported viscosity values with available literature data for *n*-octane and isooctane covering limited pressure and temperature ranges shows that the average absolute percent deviation (AAPD) varies between 1.0% and 2.5%. The data are correlated by a non-linear surface fit as a simultaneous function of temperature and pressure that yields AAPD values of 0.6% and 0.8% for *n*-octane and isooctane, respectively. The viscosity data are also correlated with a model suitable for use in reservoir simulators; the free volume theory model with density values obtained from the Peng–Robinson equation of state (PR EoS), the volume-translated PR EoS (VT-PR EoS), the perturbed chain statistical associating fluid theory (PC-SAFT EoS), and the PC-SAFT EoS in which the parameters are fit to high temperature, high pressure density data (HTHP PC-SAFT EoS). If the parameters of the free volume theory model are fit with the EoS incorporated into the model, comparable results are obtained with each of the density models. However, if the parameters of the free volume theory model are first fit using experimental density data and then an EoS is incorporated into the free volume theory model, the best viscosity results are obtained with the most accurate density models, which are the HTHP PC-SAFT and VT-PR EoS.

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1. Introduction

Viscosity data of pure hydrocarbons and mixtures over wide ranges of temperature and pressure are required in many petroleum reservoir applications, including accurate assessment of the amount of recoverable petroleum within a reservoir, the calculation of flow rates in porous media or wellbores, and the determination of the mobility ratio of a displacement process. Despite the importance of viscosity data in the petroleum industry, experimental viscosity data for many hydrocarbons are scarce, particularly at extremely high-temperature, high-pressure (HTHP) conditions up to 530 K and 240 MPa. These conditions are typically encountered in ultra-deep petroleum reservoirs, such as those

found beneath the Gulf of Mexico. Because the hydrocarbons produced from these HTHP ultra-deep formations experience significant reductions in temperature and pressure during recovery, it is highly desirable to develop a viscosity database covering the entire temperature and pressure ranges associated with the recovery process. These data can then be used to develop reliable and accurate viscosity models for reservoir simulation.

In this study, a windowed, variable-volume, rolling-ball viscometer is used to conduct viscosity measurements for *n*-octane and isooctane at pressures to ~245 MPa and temperatures to ~525 K. These data extend the pressure and temperature ranges of the available literature data for these hydrocarbons. The results are fit to an empirical 10-parameter surface fitting function that correlates the viscosity of pure components to temperature and pressure. Isothermal viscosity data are also represented as a function of pressure by an expression similar in form to the Tait equation. Experimental viscosity data generated in this study are also modeled with the free volume theory (FVT) [1] to provide a

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modeling tool for reservoir simulators capable of estimating the viscosity of multi-component mixtures. Because the FVT model requires fluid density as an input, HTHP density values are determined with the Peng–Robinson (PR EoS) [2], the volume-translated PR EoS (VT-PR EoS) [3], and the perturbed chain statistical associating fluid theory (PC-SAFT EoS) models [4]. The viscosity data and modeling results presented here complement the results reported earlier for *n*-hexadecane, *n*-octadecane, and *n*-eicosane [5].

2. Experimental

2.1. Materials

Table 1 lists the material information and thermophysical properties of *n*-octane and isooctane. Both were obtained from Sigma–Aldrich and used without further purification.

2.2. Rolling-ball viscometer details

The windowed, variable-volume, rolling-ball viscometer used to measure HTHP viscosity is described in detail elsewhere [5,7,8] and only the main features are described here. The viscometer, constructed from Inconel 718, has an inside diameter (ID) of 1.5875 cm and a maximum working volume of 50 cm³. Two balls [Industrial Tectonics Inc.], made of Inconel 718 (to minimize the effects of temperature on the calibration constant) are used in this study: one has a diameter of 1.5846 cm (99.817% of the viscometer ID) and the other has a diameter of 1.5796 cm (99.502% of the viscometer ID). A borescope is positioned against the window at the front end of the viscometer to confirm that only a single fluid phase exits and to verify that the ball is continuously rolling rather than sliding or becoming momentarily immobile during a measurement. The rolling speed of the ball is determined using a light detection technique similar to that used by Sawamura and Yamashita [9]. The detection system consists of a fiber optic light source (Model LSX 24B, InterTest) and fiber optic cables (Model IF23SM900, Banner Engineering Corporation) attached to small sapphire windows secured in ports located radially on the viscometer. The light is detected by optic sensors (Model R55FVWQ, Banner Engineering Corporation) interfaced with a computer through a LabVIEW program to measure the roll time of a ball through one set of opposing ports. The desired operating pressure is obtained using a high-pressure generator (Model 37-5.75-60, High Pressure Equipment Company) to compresses water that moves a floating piston sealed with an o-ring. The system pressure is measured using a pressure transducer (Model 345-BWS, Viatran Corporation) calibrated against a Heise pressure gauge (Model CM, 414 MPa ± 0.40 MPa, Heise Corporation). The observed temperature variation for each reported isotherm is within 0.3 K.

The working equation for the calibration constant, *k*, of a rolling-ball viscometer is [5]

$$k = \frac{\mu \cdot v}{(\rho_b - \rho_f) \sin \theta} \quad (1)$$

where *k* has units of (cm⁴ m⁻¹ s⁻²), μ is the viscosity (mPa s), *v* is the terminal velocity (cm/s) of the rolling ball, and ρ_b and ρ_f are

the ball density and fluid density (g/cm³), respectively, and θ is the angle of inclination measured with a digital protractor (Model Pro 3600, Applied Geomechanics). The viscometer is calibrated over the entire temperature and pressure ranges of interest to account for the influence of high temperature and pressure on the ball diameter and viscometer ID. Rolling-ball viscometers are typically calibrated with pure fluids. As described in our earlier work [5], the viscometer is calibrated with pure *n*-decane. Viscosity data for *n*-decane are obtained from NIST Chemistry WebBook [10], which implements a viscosity correlation proposed by Huber, Laesecke, and Xiang [11]. Density data are obtained from NIST Chemistry WebBook [10] and are compared against the densities reported by Liu et al. [12] and found to have an estimated uncertainty of 0.3%.

3. Experimental results and discussions

The density values of *n*-octane and isooctane required to solve for viscosity values using Eq. (1) are obtained with Eq. (2), a modified Tait equation [13].

$$\frac{\rho - \rho_0}{\rho} = C \log_{10} \frac{p + B}{p_0 + B} \quad (2)$$

where ρ is density, *p* is pressure, ρ_0 is density at $p_0 = 0.1$ MPa, and *B* and *C* are parameters for an isotherm determined by fitting Eq. (2) to HTHP density data reported by Liu et al. [12]. The calibration PVT data employed for the viscosity measurements cover temperatures to 522 K and pressures to 277 MPa. *C* is a temperature-independent constant. The following equations are used to determine the values of ρ_0 and *B* at a given temperature *T*:

$$\rho_0 = \sum_i^2 a_i T^i \quad (3)$$

$$B = \sum_i^2 b_i T^i \quad (4)$$

The coefficients a_i and b_i are listed in Table 2. The average absolute percent deviation (AAPD) shown in Table 2 refers to the deviation of the experimental densities reported by Liu et al., $\rho_{i,exp}$, from values calculated with the modified Tait equation, $\rho_{i,corr}$.

$$AAPD = \frac{1}{n} \sum_{i=1}^n \left| \frac{\rho_{i,exp} - \rho_{i,corr}}{\rho_{i,exp}} \right| \cdot 100 \quad (5)$$

Table 2

Parameters for the best fit of the modified Tait equation for *n*-octane and isooctane high temperature-high pressure density data obtained in [12].

Coefficient	<i>n</i> -Octane	Isooctane
a_0 (kg m ⁻³)	1104	1155
a_1 (kg m ⁻³ K ⁻¹)	-1.576	-1.840
a_2 (kg m ⁻³ K ⁻²)	7.422×10^{-4}	1.021×10^{-3}
b_0 (MPa)	353.4	311.8
b_1 (MPa K ⁻¹)	-1.372	-1.229
b_2 (MPa K ⁻²)	1.353×10^{-3}	1.226×10^{-3}
<i>C</i>	0.20	0.20
AAPD	0.1	0.2

Table 1

Material information and thermophysical properties of *n*-octane and isooctane (2,2,4-trimethylpentane). *M* (molecular mass), *T_c* (critical temperature), *P_c* (critical pressure), ω (acentric factor) [6].

Compound	CAS No.	Lot No.	Purity (wt%)	<i>M</i> (g mol ⁻¹)	<i>T_c</i> (K)	<i>P_c</i> (MPa)	ω
<i>n</i> -Octane	111-65-9	SHBC8894V	≥99.0	114.2	568.7	2.49	0.399
Isooctane	540-84-1	SHBD6018V	99.8	114.2	543.9	2.57	0.304

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