Viscosity and Density of Carbon Dioxide + 2,6,10,15,19,23-Hexamethyltetracosane (Squalane)[†]

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The viscosity and density of mixtures of carbon dioxide and 2,6,10,15,19,23-hexamethyltetracosane (squalane) are reported. The measurements were carried out using a vibrating wire instrument over a range of temperatures from (303.15 to 448.15) K and at pressures ranging from approximately the minimum miscibility pressure at a given composition to 170 MPa. Pure squalane and three different mixtures, with mole fractions of CO_2 of 0.423, 0.604, and 0.788, were investigated. The estimated expanded relative uncertainties of the measurements were ± 2 % for viscosity and ± 0.2 % for density with a coverage factor of 2. The data for each composition were correlated by simple expressions with an absolute average relative deviation less than 2 % for viscosity and less than 0.2 % for density. The results show that the addition of CO_2 to squalane at a given pressure and temperature reduces greatly the viscosity and increases slightly the density. A hard-sphere model, adjusted to fit the viscosity data of the pure substances but containing no adjustable binary parameters, was tested against the experimental data. Relative deviations bounded by approximately ± 60 % were found.

Introduction

Mixtures of carbon dioxide and long-chain hydrocarbons are important in at least two major fields of engineering. First, in the context of refrigeration engineering, these mixtures arise in industrial cooling plants utilizing CO_2 as the working fluid. Carbon dioxide as a refrigerant has good environmental performance,[1] with zero ozone depletion potential and low global warming potential. Moreover, its favorable thermophysical properties and nontoxic nature render CO_2 an excellent working fluid for many industrial refrigeration applications. To design effective and efficient refrigeration equipment, it is necessary to know some of the key thermophysical properties of the working fluid and, importantly, of its mixtures with compressor lubricants. Mixtures containing 2,6,10,15,19,23-hexamethyltetracosane (squalane) are of interest because this branched alkane is representative of the paraffinic components of the mineral oils that are typically used as compressor lubricants when CO_2 is the working fluid. The viscosity of the mixture is a key parameter both in assessing the suitability of a refrigerant–lubricant system and in the design of equipment.[2] Thus, obtaining experimental data for such properties is important and, because of the high pressures reached locally in the lubricant films surrounding moving parts, data are required at pressures considerably beyond the normal maximum cycle pressures of (15 to 20) MPa.[3]

Second, carbon dioxide has been used to a limited extent for several decades to enhance oil recovery (EOR) from mature reservoirs, and beneficial effects have been observed.[4,5] With demand rising, and supplies of easily extracted oil in decline, the economics of CO_2-EOR may turn more strongly in its favor. Furthermore, it is possible that CO_2 capture from fossil-fuel combustion processes will be implemented on a massive scale with the CO_2 ultimately being stored long-term in depleted petroleum reservoir formations. Optimizing the various processes involved in both CO_2-EOR and oilfield storage of CO_2 will require knowledge of the viscosity and density (along with phase behavior and interfacial tension) of mixtures containing CO_2 and hydrocarbons. To fully understand the interaction of CO_2 and the plethora of molecules that make up reservoir fluids, it is necessary to obtain some information on thermophysical properties of CO_2 and long-chain hydrocarbons. Although squalane is a minor constituent of reservoir fluids, there are a number of reasons why it is a natural choice for modeling long-chain hydrocarbons. Heavier oils are usually characterized in terms of pseudo components, and often one of these is a C_{30} fraction. The branched nature of the molecule ensures that squalane remains in the liquid state at temperatures and pressures of interest. Finally, high-purity squalane is available commercially.

The wide range of conditions of interest, of relevance to engineering applications, precludes obtaining viscosity and density of relevant mixtures by experimental means alone and calls for reliable and accurate prediction methods. However, the viscosity of dense-fluid mixtures is difficult to predict, especially when one has mixtures containing both large and small molecules. There is an ongoing effort to develop and validate more reliable models for this property[6,7] and a commensurate need for experimental data on representative mixtures. The present study is aimed at providing such data for a simple model system containing CO_2 and the branched alkane 2,6,10,15,19,23-hexamethyltetracosane.

Previous studies of CO_2 (1) + squalane (2) include measurement of the phase diagram over the full composition range at temperatures between (278 and 423) K and at pressures up to

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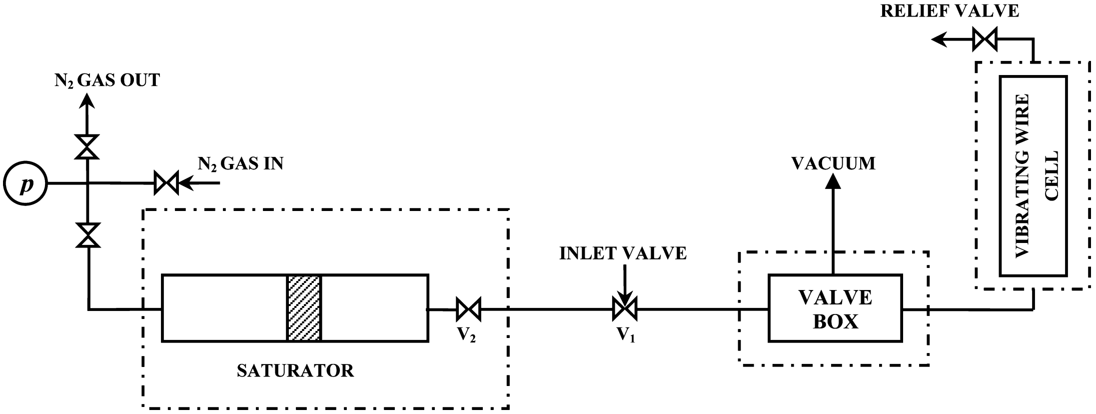

Figure 1. Schematic of the experimental apparatus. Dashed boxes represent temperature-controlled areas, and circled p denotes the pressure transducer.

100 MPa.[8] Additional solubility data of squalane in dense liquid carbon dioxide have also been reported.[9] The viscosity of the mixture has been studied previously in the composition range $0 \le x_1 \le 0.417$ at $293 \le T/\mathrm{K} \le 353$ and $p \le 20$ MPa.[10] In addition, the viscosity of pure squalane has been studied by Pensado et al.[11] at $303 \le T/\mathrm{K} \le 353$ and $p \le 60$ MPa, by Bair[12] at $313 \le T/\mathrm{K} \le 373$ and $p \le 1300$ MPa, by Bair[13] at $293 \le T/\mathrm{K} \le 373$ and $p \le 1200$ MPa, and by Krahn and Luft at $298 \le T/\mathrm{K} \le 453$ and $p \le 200$ MPa.[14] Finally, the density of pure squalane has been reported by Pensado et al.[15] In the present study, simultaneous measurements of density and viscosity have been made at $303.15 \le T/\mathrm{K} \le 448.15$, $p \le 170$ MPa, and $0 \le x_1 \le 0.8$.

Experimental Procedure

The squalane (mass fraction $w \ge 0.99$) was obtained from Sigma Aldrich; octane ($w \ge 0.995$) was obtained from Fluka; liquid viscosity standard N75 was obtained from Cannon Instrument Company; and the CO_2 (mole fraction purity $x \ge 0.99995$) was obtained from BOC. All were used without further purification. The measurements were performed using a vibrating-wire apparatus that serves to determine simultaneously both viscosity and density.[16−18] The gold-plated tungsten wire of length 70 mm and diameter 0.1 mm was suspended vertically in the fluid, between the poles of a permanent magnet, and was tensioned by an aluminum sinker of mass 0.17 kg. An alternating current was passed through the wire, thereby setting it into transverse oscillation, and the emf developed across the wire was measured by means of a lock-in amplifier. This emf generally comprises two components: the first is simply the voltage developed across the electrical impedance presented by the stationary wire, while the second is the induced voltage arising from the motion of the wire through the fluid. The frequency response of the oscillating wire was measured in the vicinity of the fundamental transverse resonance mode. The resonance frequency of this mode is sensitive to the density of the surrounding fluid, largely as a consequence of the buoyancy effect exerted on the sinker and the resulting changes in the tension of the wire. The width of the resonance curve is sensitive to the viscosity of the fluid. Both effects are described accurately by a fully developed working equation for the instrument.[17,19,20]

The use of gold-plated wires was found to be advantageous in previous work on diesel fuels where the plating clearly inhibited a degradation reaction in the fluid that had been observed at elevated temperatures when bare tungsten wires were used. In the present case, the plating was probably unnecessary.

The temperature of the fluid was inferred from the reading of a platinum resistance thermometer that was mounted in a well in the cap of the pressure vessel. This thermometer was calibrated by comparison with a standard platinum resistance thermometer that had itself been calibrated on ITS-90 at the UK National Physical Laboratory. The expanded uncertainty of the temperature measurements was ± 0.02 K at a coverage factor, k, of 2. The pressure was measured in the external pipework by means of a Paroscientific transducer (model 40K-110) that had been calibrated against a pressure balance in the range (0.1 to 200) MPa. The expanded uncertainty of pressure was ± 0.02 MPa ($k = 2$).

The working equations of the instrument contain four quantities that we choose to determine by calibration. The resonance frequency and logarithmic decrement of the wire under vacuum were inferred from measurements in ambient air, while the radius of the wire and the volume of the tensioning weight were obtained from a measurement in octane at $T = 298.15$ K and $p = 1.0$ MPa. The viscosity of octane under those conditions was taken to be $\eta = (0.514 \pm 0.002)$ mPa·s, based on the value at $T = 298.15$ K and $p = 0.1$ MPa, and the associated relative uncertainty of ± 0.3 %, recommended by Dymond and Øye,[21] and the pressure dependence given by the correlation of Huber et al.[22] The density of octane at $T = 298.15$ K and $p = 1.0$ MPa was taken to be $\rho = 699.1\ \mathrm{kg \cdot m^{-3}}$ from the equation of state of Span and Wagner.[23] Other quantities in the working equations were either directly measured or were material properties with values taken from the literature.[17]

As indicated in Figure 1, the apparatus comprised three main components: the saturator in which the mixture was prepared;[24] a valve box containing the pressure control and measurement devices; and the vibrating-wire cell itself.[24] All three principal components were independently temperature-controlled, and when necessary to avoid phase separation, the interconnecting tubing was heated. The saturator was a cylindrical stainless-steel pressure vessel containing a free piston with an O-ring seal. On one side of the piston, the saturator was connected to a high-pressure nitrogen supply which enabled the piston to be employed as a pump. On the other side, the saturator was fitted with an annular stainless-steel agitator ring ("doughnut") which was free to slide back and forth within the cylinder. The saturator was provided with a rocking system which was used to set the agitator ring in motion to facilitate mixing of the fluids.

The mixtures were prepared as follows. The saturator was first evacuated. Then V_1 was closed, the valve box disconnected, and the right-hand side of V_1 (see Figure 1) connected to a vessel containing the liquid hydrocarbon. Liquid was then drawn into

Table 1. Experimental Viscosity η and Density ρ of Pure Squalane

p / MPa	η / (mPa·s)	ρ / (kg·m^{-3})	p / MPa	η / (mPa·s)	ρ / (kg·m^{-3})
	T = 303.18 K			T = 398.15 K	
1.07	22.0	802.0	5.23	2.17	746.4
5.30	24.2	803.5	25.31	2.89	763.3
15.58	30.3	806.9	56.10	4.24	783.5
25.53	36.9	813.9	85.89	5.88	799.5
35.79	44.3	826.5	115.45	7.93	812.6
45.77	54.6	825.1	145.82	10.6	824.7
55.77	66.3	825.9	176.10	13.8	835.4
5.74	24.4	804.4	5.16	2.17	746.3
	T = 348.13 K			T = 448.25 K	
5.27	5.59	776.9	5.58	1.17	716.3
25.49	7.79	790.6	25.47	1.54	736.8
56.28	12.3	807.7	55.51	2.17	759.9
85.86	18.4	821.2	85.62	2.89	778.7
115.83	26.9	832.6	115.51	3.76	793.3
145.93	38.7	844.3	145.58	4.78	806.4
175.12	55.6	843.2	176.05	5.99	818.2
5.29	5.60	777.0	5.73	1.18	716.5

the saturator through valve V_1. The amount of hydrocarbon introduced was determined by carefully weighing the sample vessel before and after the transfer. The CO_2 supply was then connected to the inlet of V_1 and gas admitted, thereby pushing the hydrocarbon fully into the saturator vessel. The addition of CO_2 was monitored by continuous weighing of the gas bottle, but the precise amount was determined from careful weighing of the uncoupled bottle before and after the transfer. The amount of CO_2 lost in the dead volume between the bottle and V_2 was determined by means of additional weighing operations. An electronic balance with a resolution of 0.001 g was employed for the all weighing, and based on this factor, the expanded uncertainty in mole fraction was ± 0.0001 with a coverage factor of 2.

After introducing the components, the pressure and the temperature of the saturator were adjusted to bring the mixture to the single-phase region,[8] and homogenization was achieved by rocking the saturator for at least 12 h. The saturator was then reconnected to the valve box through which the mixture was delivered to the vibrating-wire cell in which the measurements took place. To keep the fluid above the minimum miscibility pressure during the transfer, the valve box and vibrating-wire cell were first pressurized with nitrogen. A greater pressure was then applied to the gas side of the saturator, and the mixture was pushed through into the cell with the nitrogen venting through the relief valve atop the cell. To ensure that all the nitrogen was expelled from the system, including that which dissolved at the interface between the gas and the advancing liquid, a small quantity of mixture of (about 15 mL) was also discharged from the relief valve.

Results

Four different compositions of CO_2 (1) + squalane (2) were studied with x_1 = (0, 0.4233, 0.6039, and 0.7882). The viscosity and density of each mixture were measured along isotherms at nominal temperatures of (303.15, 348.15, 398.15, and 448.15) K, with pressures generally up to 170 MPa. The results are given in Tables 1 to 4. The actual experimental temperatures, given in Tables 1 to 4, differed slightly from the nominal values but were constant to ± 0.02 K during a given isotherm. In the case of pure squalane along the isotherm at T = 303.18 K, data were gathered up to only p = 55 MPa, beyond which the viscosity exceeded that which could be measured sensitively with the 0.1 mm diameter wire fitted to the instrument.

Table 2. Experimental Viscosity η and Density ρ of CO_2 (1) + Squalane (2) at x_1 = 0.4233

p / MPa	η / (mPa·s)	ρ / (kg·m^{-3})	p / MPa	η / (mPa·s)	ρ / (kg·m^{-3})
	T = 303.18 K			T = 398.31 K	
10.07	9.17	815.3	10.83	1.39	755.3
170.21	85.9	882.8	170.00	6.24	845.0
150.08	67.8	869.4	150.52	5.40	837.2
130.28	52.3	867.8	130.35	4.62	828.4
110.38	40.1	862.1	110.29	3.92	819.1
90.25	30.5	856.5	90.45	3.30	808.9
70.40	23.0	849.3	70.50	2.74	797.4
50.51	17.3	839.2	50.35	2.24	784.0
30.38	12.7	828.0	30.18	1.79	768.1
10.06	9.12	814.8	10.79	1.38	749.0
	T = 348.25 K			T = 448.35 K	
10.07	2.99	783.6	11.57	0.81	720.6
169.67	17.3	866.3	169.90	3.28	824.8
150.67	14.5	859.3	150.51	2.88	816.5
130.40	11.9	851.3	130.44	2.52	807.0
110.61	9.83	842.8	110.31	2.17	796.6
90.61	7.98	833.7	90.67	1.86	785.2
70.53	6.42	823.5	70.45	1.57	771.8
50.59	5.10	812.2	50.41	1.30	756.5
30.44	3.95	799.2	30.33	1.04	737.6
10.10	2.98	783.4	11.45	0.80	715.2

Table 3. Experimental Viscosity η and Density ρ of CO_2 (1) + Squalane (2) at x_1 = 0.6039

p / MPa	η / (mPa·s)	ρ / (kg·m^{-3})	p / MPa	η / (mPa·s)	ρ / (kg·m^{-3})
	T = 303.18 K			T = 398.13 K	
10.60	4.92	823.9	10.94	1.01	749.2
30.81	6.58	838.1	30.87	1.30	771.8
50.82	8.58	850.4	50.55	1.61	789.2
70.80	11.0	861.0	70.81	1.95	804.2
91.10	14.0	871.1	91.23	2.31	817.2
100.67	15.6	874.8	110.70	2.69	828.2
111.11	17.5	879.9	131.24	3.12	838.7
130.85	21.7	888.1	150.74	3.57	847.7
150.50	26.5	897.9	170.66	4.08	856.2
170.44	32.0	910.5	11.10	1.00	748.9
	T = 348.11 K			T = 448.13 K	
10.48	1.92	788.1	10.63	0.69	713.1
30.31	2.49	806.0	30.73	0.89	739.7
50.27	3.13	820.7	50.59	1.09	759.8
70.18	3.85	833.3	70.38	1.22	776.6
90.32	4.68	844.4	91.38	1.43	791.8
110.88	5.64	854.6	111.05	1.63	804.5
130.86	6.70	863.7	130.81	1.84	815.7
150.87	7.90	872.1	150.96	2.08	826.0
170.91	9.28	879.8	171.00	2.35	835.3
10.45	1.92	787.7	11.01	0.68	713.3

For states with $\eta \leq 30$ mPa·s, the expanded relative uncertainties of the measurement were estimated to be ± 2 % for viscosity and ± 0.2 % for density, with $k = 2$. For $\eta > 30$ mPa·s, the relative uncertainty of the density increased rapidly, while that of the viscosity increased slowly. This behavior arises from the fact that ρ and η increasingly become correlated in the analysis of the measured resonance curves as they broaden at high viscosities. This regime was entered for a few of the state points investigated. We estimate that the relative uncertainty of η increases from ± 2 % at η = 30 mPa·s to ± 3 % at η = 90 mPa·s, while the relative uncertainty of ρ increases from ± 0.2 % to ± 0.8 % over the same range. A check measurement at low pressure was made at the end of each isotherm cycle to monitor whether the properties of the fluids had changed during the experiment. Generally, these check measurements were satisfactory, and the density and the viscosity agreed within the expected repeatabilities of ap-

Table 4. Experimental Viscosity η and Density ρ of CO_2 (1) + Squalane (2) at $x_1 = 0.7882$

p/MPa	η/(mPa·s)	ρ/(kg·m^{-3})	p/MPa	η/(mPa·s)	ρ/(kg·m^{-3})
	$T = 303.17$ K			$T = 398.33$ K	
30.19	2.36	854.3	30.15	0.62	760.4
170.57	8.13	934.8	170.31	1.84	873.6
151.34	6.94	922.8	150.62	1.65	863.2
130.57	5.91	911.0	130.55	1.46	851.6
110.64	4.95	901.1	110.76	1.28	839.0
90.49	4.15	890.0	90.51	1.10	824.2
70.73	3.43	877.8	70.58	0.94	807.3
50.10	2.79	863.4	50.50	0.78	786.7
30.74	2.24	847.4	30.50	0.62	759.9
	$T = 348.25$ K			$T = 448.41$ K	
30.61	1.07	806.9	30.16	0.41	714.5
170.31	3.34	902.0	169.72	1.22	847.5
150.60	2.94	892.7	150.48	1.10	836.2
130.53	2.57	882.3	130.36	0.97	823.3
110.35	2.22	870.8	110.59	0.85	809.1
90.68	1.91	858.4	90.42	0.74	792.3
70.65	1.61	844.0	70.35	0.63	772.5
50.54	1.34	827.0	50.45	0.52	748.0
30.39	1.08	806.0	30.82	0.41	714.9

proximately $10^{-3}\rho$ and $10^{-2}\eta$, respectively, after allowing for small differences in pressure between the initial and final measurements. However, for the isotherms at $T = (398.31$ and $348.35)$ K with $x_1 = 0.4233$ (Table 2) and for the isotherm at $T = 303.17$ K with $x_1 = 0.7882$ (Table 4), the check measurements indicate that the density had changed by an amount in excess of the expected repeatability but not more than $7 \cdot 10^{-3}\rho$. This suggests that a partial demixing might have occurred upon expansion, but we do not have a detailed explanation. Hence, for those measurements, a higher relative uncertainty in density of about 0.7 % should be considered.

The measurements were performed initially with increasing pressures (for pure squalane and the mixture composition $x_1 = 0.6039$) and later (for the other compositions) with decreasing pressure. This change of approach, from pressure increments to pressure decrements, was related to the fact that CO_2 dissolves in elastomeric seals leading to swelling and possibly to fragmentation during decompression. The equipment used a Viton rubber O-ring as the seal on the main vessel and additional Viton O-rings to seal the saturator vessel and the floating piston within it. O-ring damage appeared to be related to the rate of decompression. Hence it was felt preferable to first compress the mixture to the maximum pressure and then to make the measurements with pressure reducing. This resulted in much smaller pressure decrements separated by equilibration periods of about 1 h and appeared to lead to longer seal life.

The typical dependency of the viscosity on temperature and pressure is shown in Figure 2 for $x_1 = 0.4233$. The data are plotted on a semilogarithmic scale and show the expected behavior in which viscosity increases with pressure and decreases with temperature. Figure 3 and Figure 4 show the dependency of viscosity and density, respectively, upon the composition. The results show clearly that dissolution of CO_2 in the squalane leads to both a dramatic reduction in the viscosity and a small increase in the density. The increased uncertainty in ρ when $\eta > 30$ mPa·s is evident in the increased scatter seen in Figure 4 for pure squalane at the higher pressures.

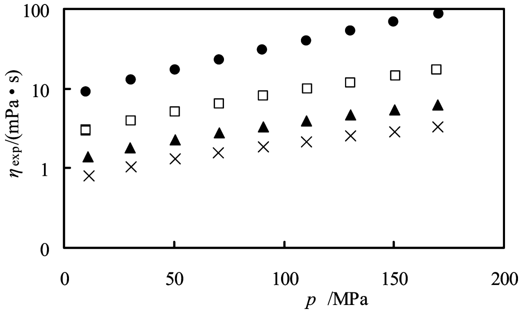

Figure 2. Experimental viscosities η_{exp} of CO_2 (1) + squalane (2) at $x_1 = 0.4233$ as a function of pressure p: ●, $T = 303.15$ K; □, $T = 348.15$ K; ▲, $T = 398.15$ K; ×, $T = 448.15$ K.

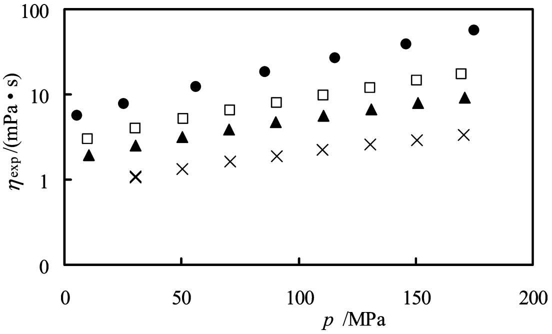

Figure 3. Experimental viscosity η_{exp} of CO_2 (1) + squalane (2) at $T = 348.15$ K as a function of pressure p: ●, $x_1 = 0$; □, $x_1 = 0.4233$; ▲, $x_1 = 0.6039$; ×, $x_1 = 0.7882$.

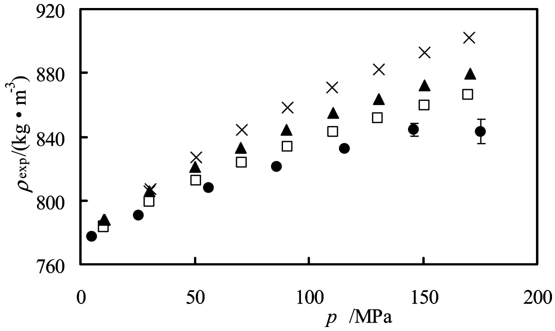

Figure 4. Experimental density ρ_{exp} of CO_2 (1) + squalane (2) at $T = 348.15$ K as a function of pressure p: ●, $x_1 = 0$; □, $x_1 = 0.4233$; ▲, $x_1 = 0.6039$; ×, $x_1 = 0.7882$. Error bars are shown only where they exceed the size of the plotting symbols.

The present measurements span the range $0.4 \leq \eta/(\text{mPa}\cdot\text{s}) \leq 66$, while the wire radius was determined by calibration in a fluid with $\eta \approx 0.5$ mPa·s. As a check on the performance of the instrument in an extended range of viscosity, we measured the viscosity and density of the commercially available standard reference liquid N75 at $p = 0.1$ MPa and $T = 322.26$ K. The measured viscosity of 41.5 mPa·s was found to have a relative deviation of −2 % from the reference data provided by the manufacturer, while the relative deviation of the density was 0.01 %.

Table 5. Coefficients of Equations 1 to 3 for Viscosity and Statistical Parameters

coefficient	$x_1 = 0$	$x_1 = 0.4233$	$x_1 = 0.6039$	$x_1 = 0.7882$
A_η	$-2.62 \cdot 10^0$	$-3.28 \cdot 10^0$	$-2.48 \cdot 10^0$	$-4.42 \cdot 10^0$
B_η	$7.50 \cdot 10^2$	$9.32 \cdot 10^2$	$5.62 \cdot 10^2$	$1.29 \cdot 10^3$
C_η	$-1.72 \cdot 10^2$	$-1.28 \cdot 10^2$	$-1.60 \cdot 10^2$	$-4.11 \cdot 10^1$
d_0	$-5.94 \cdot 10^{-1}$	$2.54 \cdot 10^1$	$4.99 \cdot 10^0$	$1.37 \cdot 10^1$
d_1	$-1.39 \cdot 10^3$	$-2.12 \cdot 10^4$	$-4.96 \cdot 10^3$	$-1.11 \cdot 10^4$
d_2	$1.20 \cdot 10^6$	$4.77 \cdot 10^6$	$1.47 \cdot 10^6$	$2.51 \cdot 10^6$
e_0	$7.07 \cdot 10^2$	$3.36 \cdot 10^3$	$1.71 \cdot 10^3$	$3.15 \cdot 10^3$
e_1	$-8.25 \cdot 10^{-1}$	$-1.47 \cdot 10^1$	$-6.75 \cdot 10^0$	$-1.39 \cdot 10^1$
e_2	$-8.70 \cdot 10^{-4}$	$1.68 \cdot 10^{-2}$	$6.95 \cdot 10^{-3}$	$1.58 \cdot 10^{-2}$
$10^2\Delta_{AAD,\eta}$	0.80	0.43	0.77	1.41
$10^2\Delta_{MAD,\eta}$	1.97	1.31	3.70	4.08
$10^2\Delta_{Bias,\eta}$	0.13	0.10	0.12	−0.06

Correlation

The data have been correlated using simple relations that take pressure and temperature as the independent variables. The viscosity was correlated by the expression[25]

$$\eta = A_\eta \exp\left(\frac{B_\eta}{T + C_\eta}\right)\left(\frac{p + E}{p_0 + E}\right)^D \tag{1}$$

where A_η, B_η, and C_η are constants, $p_0 = 0.1$ MPa, and D and E are functions of temperature as follows

$$D = \sum_{i=0}^{2} d_i(\mathrm{K}/T)^i \tag{2}$$

$$E/\mathrm{MPa} = \sum_{i=0}^{2} e_i(T/\mathrm{K})^i \tag{3}$$

As described previosuly,[16] the parameters of these equations were determined by a nonlinear optimization that minimized the absolute average relative deviation defined for a property X by

$$\Delta_{\mathrm{AAD},X} = \frac{1}{N}\sum_{i=1}^{N}\left(\frac{|X_i - X_{i,\mathrm{fit}}|}{X_i}\right) \tag{4}$$

Here, X_i is an experimental datum, $X_{i,\mathrm{fit}}$ is calculated from the correlation applied at the same state point, and N is the total number of points. We also calculated the maximum absolute relative deviation ($\Delta_{\mathrm{MAD},X}$) and the relative bias ($\Delta_{\mathrm{bias},X}$) where

$$\Delta_{\mathrm{MAD},X} = \mathrm{Max}\left(\frac{|X_i - X_{i,\mathrm{fit}}|}{X_i}\right) \tag{5}$$

$$\Delta_{\mathrm{Bias},X} = \frac{1}{N}\sum_{i=1}^{N}\frac{(X_i - X_{i,\mathrm{fit}})}{X_i} \tag{6}$$

The fitting procedure was applied individually to each mixture composition, and the parameters obtained are given in Table 5 together with the fitting statistics.

The density was correlated by the modified Tait equation[26]

$$\rho = \rho_0\left[1 - C\log_{10}\left(\frac{p + B}{p_0 + B}\right)\right]^{-1} \tag{7}$$

where $p_0 = 0.1$ MPa as before, ρ_0 is the density at $p = p_0$, C is a constant, and B is a temperature-dependent parameter. In the present work, ρ_0 and B have been correlated as follows

$$B/\mathrm{MPa} = \sum_{i=0}^{2} b_i(T/\mathrm{K})^i \tag{8}$$

$$\rho_0/(\mathrm{kg{\cdot}m^{-3}}) = \sum_{i=0}^{2} a_i(T/\mathrm{K})^i \tag{9}$$

Again, the parameters were adjusted in a nonlinear optimization to minimize the absolute average relative deviation, and the results are given in Table 6.

Table 6. Coefficients of Equations 7 to 9 for Density and Statistical Parameters

coefficient	$x_1 = 0$	$x_1 = 0.4233$	$x_1 = 0.6039$	$x_1 = 0.7882$
a_0	$9.79 \cdot 10^{2}$	$9.97 \cdot 10^{2}$	$1.13 \cdot 10^{3}$	$1.01 \cdot 10^{3}$
a_1	$-5.47 \cdot 10^{-1}$	$-5.32 \cdot 10^{-1}$	$-1.17 \cdot 10^{0}$	$-1.33 \cdot 10^{-1}$
a_2	$-1.25 \cdot 10^{-4}$	$-2.84 \cdot 10^{-4}$	$4.66 \cdot 10^{-4}$	$-1.66 \cdot 10^{-3}$
b_0	$4.77 \cdot 10^{2}$	$5.04 \cdot 10^{2}$	$5.06 \cdot 10^{2}$	$3.66 \cdot 10^{2}$
b_1	$-1.72 \cdot 10^{0}$	$-1.82 \cdot 10^{0}$	$-1.83 \cdot 10^{0}$	$-1.47 \cdot 10^{0}$
b_2	$1.65 \cdot 10^{-3}$	$1.76 \cdot 10^{-3}$	$1.79 \cdot 10^{-3}$	$1.49 \cdot 10^{-3}$
C	$1.78 \cdot 10^{-1}$	$2.09 \cdot 10^{-1}$	$2.47 \cdot 10^{-1}$	$2.03 \cdot 10^{-1}$
$10^2\Delta_{\mathrm{AAD},\rho}$	0.14	0.15	0.14	0.10
$10^2\Delta_{\mathrm{MAD},\rho}$	0.83	0.79	0.59	0.62
$10^2\Delta_{\mathrm{Bias},\rho}$	0.00	0.00	−0.04	0.00

The quality of the correlations is illustrated by example deviation plots for viscosity (Figure 5) and density (Figure 6), both of which relate to the composition $x_1 = 0.4233$. These indicate that, while there is evidence of some systematic deviations in viscosity, the correlating equations are able to fit the data to within their estimated uncertainties. The statistical measures summarized in Table 5 and Table 6 show that this is typical of the whole data set.

Comparison with Literature

In Figure 7 and Table 7, we compare the available literature data for the viscosity of squalane[10−14] with eq 1. Tomida et al.[10] used a rolling ball viscometer calibrated at $T = 298.15$ K

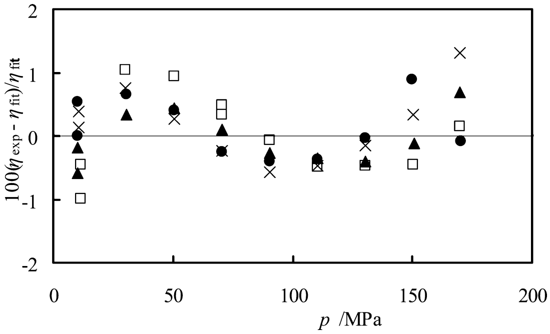

Figure 5. Fractional deviation of the viscosity of CO_2 (1) + squalane (2) from eq 1 at $x_1 = 0.4233$ as a function of pressure p: ●, $T = 303.15$ K; ▲, $T = 348.15$ K; ×, $T = 398.15$ K; □, $T = 448.15$ K. The relative uncertainty of the correlation is the same as the scale of the plot.

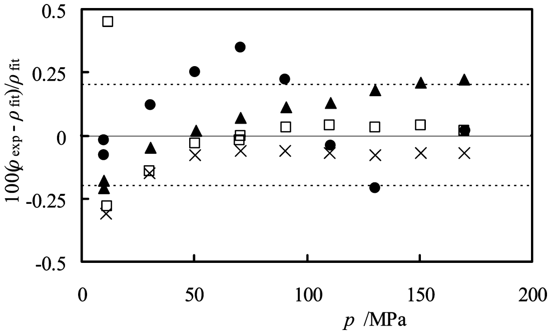

Figure 6. Fractional deviation of the density of CO_2 (1) + squalane (2) from eq 7 at $x_1 = 0.4233$ as a function of pressure p: ●, $T = 303.15$ K; ▲, $T = 348.15$ K; ×, $T = 398.15$ K; □, $T = 448.15$ K; - - -, relative uncertainty of eq 7.

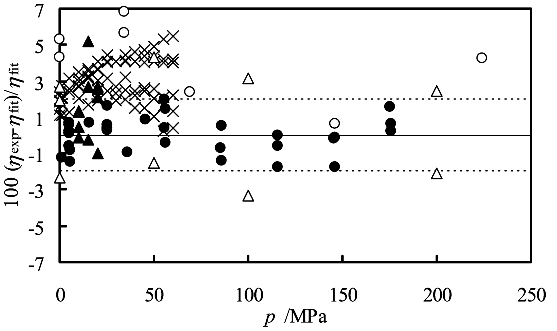

Figure 7. Fractional deviation of the viscosity of squalane from eq 1 as a function of pressure p: ●, This work; ▲, Tomida et al.;[10] ×, Pensado et al.;[11] ○, Bair (2002);[12] △, Bair (2006);[13] - - -, relative uncertainty of eq 1.

Table 7. Deviation of Literature Viscosity Data for Squalane from Equation 1

source	$10^2\Delta_{AAD,\eta}$	$10^2\Delta_{Bias,\eta}$	$10^2\Delta_{MAD,\eta}$
Tomida et al.[10]	1.6	1.4	5.2
Pensado et al.[11]	2.9	2.9	5.5
Bair[12]	4.2	4.2	6.8
Bair[13]	3.1	1.3	7.4
Krahn and Luft[14]	13.3	13.3	21.1

and $p = 0.1$ MPa with commercially available standard reference liquids. The calibration constant of the viscometer at other conditions was determined from a physical model, and the claimed relative uncertainty of η was ± 3 %. All but one point agrees with our eq 1 to within the combined uncertainty. Pensado et al.[11] also used a rolling ball viscometer which they calibrated with 1-phenyldodecane at each state point. Their results, which have a claimed relative uncertainty of ± 3 %, show an overall mean relative deviation of about +3 % from eq 1, while the results at $p = 0.1$ MPa have mean relative deviations of +2 %. Bair[12] used a falling body viscometer with a claimed relative uncertainty of ± 2 %; these results span the full pressure range of the present study at temperatures of (313.15 and 373.15) K. Compared with eq 1, these data also show positive relative deviations that are comparable to the combined uncertainties. Subsequent results by the same author[13] are in rather better agreement, with mean relative deviations of only +1.3 %. Seen together, these first four literature sources[10−13] exhibit a pattern of small positive relative deviations from eq 1, averaging 3 %. Krahn and Luft[14] used a rolling ball viscometer calibrated in decane and reported results with a claimed relative uncertainty of ± 2 %. However, these data (not shown in Figure 7) exhibit large positive relative deviations from eq 1 ranging up to 21 %. In the case of density, shown in Figure 8 and Table 8, the deviations of the literature data[10,15] from eq 7 average +0.15 % and are mostly within the combined uncertainties.

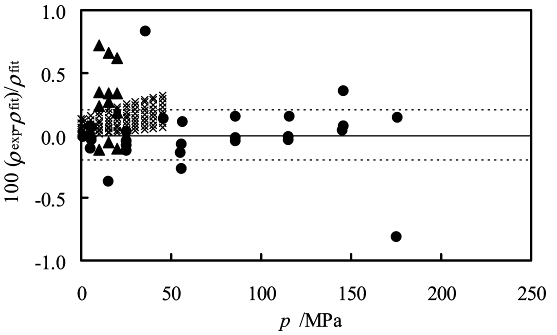

Figure 8. Fractional deviation of the density of squalane from eq 7 as a function of pressure p: ●, Tomida et al.;[10] ×, Pensado et al.;[15] - - -, relative uncertainty of eq 7.

Table 8. Deviation of Literature Density Data for Squalane from Equation 7

source	$10^2\Delta_{AAD,\eta}$	$10^2\Delta_{Bias,\eta}$	$10^2\Delta_{MAD,\eta}$
Tomida et al.[10]	0.33	0.29	0.71
Pensado et al.[15]	0.12	0.12	0.32

Comparisons with the one available literature source[10] for the viscosity and density of the mixture are more difficult to make because the reported compositions do not coincide with those of the present study. However, for the mixture with $x_1 = 0.4233$, Tomida et al.[10] report data at the nearby composition $x_1 = 0.417$, and a comparison is possible. To effect this, we used eqs 1 and 7 to obtain the viscosity and density for each of the compositions studied in this work at the temperatures and pressures given by Tomida et al.[10] We then interpolated with respect to composition to obtain values of viscosity and density with which to compare the literature data. Figures 9 and 10 show how well our model describes those results: the agreement is satisfactory as $\Delta_{AAD,\rho} < 0.1$ %, $\Delta_{AAD,\eta} < 3.5$ %, and both are within the combined uncertainties.

Modeling

It is very difficult to model accurately the viscosity of highly asymmetric mixtures such as CO_2 + squalane. Nevertheless, we consider briefly the hard-sphere model of Dymond and Assael.[27,28] In this approach, a dimensionless reduced viscosity η^* is defined such that

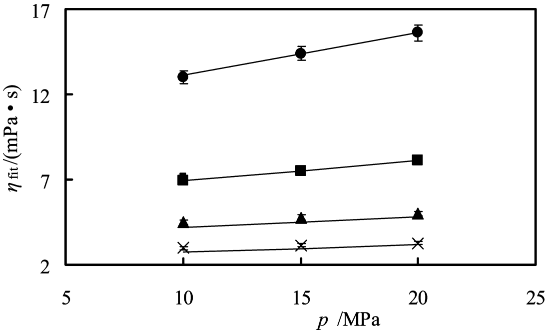

Figure 9. Comparison between the present work and the results of Tomida et al.[10] for the viscosity of CO_2 (1) + squalane (2) at $x = 0.417$. This work: —, eq 1 interpolated to $x_1 = 0.417$. Literature data:[10] ●, $T = 293.15$ K; ■, $T = 313.15$ K; ▲, $T = 333.15$ K; ×, $T = 353.15$ K.

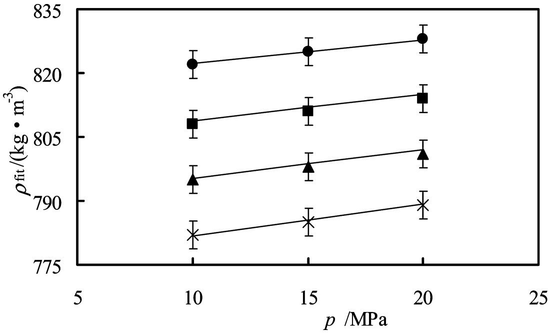

Figure 10. Comparison between the present work and the results of Tomida et al.[10] for the density of CO_2 (1) + squalane (2) at $x_1 = 0.417$. This work: —, eq 7 interpolated to $x_1 = 0.417$. Literature data:[10] ●, $T = 293.15$ K; ■, $T = 313.15$ K; ▲, $T = 333.15$ K; ×, $T = 353.15$ K.

$$\eta^* = \frac{16}{5}(2N_A)^{1/3}(\pi/MRT)^{1/2}V_m^{2/3}(\eta/R_\eta) \qquad (10)$$

where N_A is Avogadro's constant, $V_m = M/\rho$ is the molar volume, M is the molar mass, and R_η is the roughness factor, assumed constant for a given substance. It was argued that η^* should be a universal function of a reduced volume (V_m/V_0) among a conformal set of fluids sharing a common value of the roughness factor. This was indeed shown to hold for argon, krypton, and xenon in the liquid and supercritical states. Consideration of the experimental data for those substances, taking $R_\eta = 1$, established the form of the universal curve as follows[27]

$$\log_{10} \eta^* = \sum_{i=0}^{7} f_i(V_m/V_0)^{-i} \qquad (11)$$

The coefficients f_i of eq 11 have been tabulated[28] and are valid for $1.5 \leq V_m/V_0 \leq 5$. The molar "core" volume V_0 is permitted to be a function of temperature only and, for practical purposes, may be correlated by a polynomial

$$V_0/(\mathrm{cm^3 \cdot mol^{-1}}) = \sum_{i=0}^{N} g_i(T/\mathrm{K})^i \qquad (12)$$

Equations 10 to 12 may be used to correlate the viscosity of a pure substance as a function of density and temperature by adjusting the set of parameters R_η and g_i ($i = 0, N$). Then, by postulating mixing rules for R_η and V_0, the model may be used to predict the viscosity of a mixture of M components. The simplest mixing rules, which work well for the inert gases and light alkanes, are those linear in mole fraction

$$R_\eta = \sum_{i=1}^{M} x_i R_{\eta,i} \qquad (13)$$

$$V_0 = \sum_{i=1}^{M} x_i V_{0,i} \qquad (14)$$

To apply this approach, we first correlated the viscosities of both pure components in the ranges $303.15 \leq T/\mathrm{K} \leq 448.15$ and $p \leq 170$ MPa. For CO_2, we took $\eta(T, V_m)$ from the IUPAC-recommended correlation,[29] which represents the critically evaluated primary experimental data for this substance, and $V_m(T, p)$ from the equation of state of Span and Wagner.[30] After an initial analysis, the lower pressure limit considered for CO_2 was adjusted such that the only states considered were those for which $V_m/V_0 \leq 5$. Unfortunately, in the case of squalane, the analysis led to reduced volumes in the range $1.2 \leq V_m/V_0 \leq 1.5$ for which it was necessary to use eq 11 at values of V_m/V_0 lower than its stated range of validity. For both pure fluids, three terms were retained in eq 12, and the parameters obtained are given in Table 9. The model was applied to the three mixture compositions studied in this work, and the results are shown in Figure 11, along with the fit for pure squalane which is reasonable but still usually outside the experimental uncertainty. A number of the mixture states investigated were again found to correspond to $V_m/V_0 < 1.5$; nevertheless, qualitatively the model predicts the expected decline in viscosity with increasing temperature and/or CO_2 content. Quantitatively, the relative deviations from the hard sphere model are large (± 60 %). For mixtures of lower CO_2 content, specifically $x_1 \leq 0.4$, the model appears to predict the viscosity with relative deviation not worse than about ± 20 %, and this degree of uncertainty may well be acceptable in connection with modeling of EOR processes. Although the model is sensitive to the molar volume, the large deviations found are not attributable to plausible errors in that quantity. For example, changing the molar volume by the typical experimental uncertainty of 0.2 % resulted in a change in the predicted viscosity of about 3 % for all states.

Table 9. Parameters of Equations 10 to 12 for the Viscosity of the Pure Fluids

substance	CO_2	squalane
R_η	0.94015	8.0416
g_0	25.802	631.293
g_1	−0.025251	−0.95450
g_2	$1.7948 \cdot 10^{-5}$	$9.0351 \cdot 10^{-4}$
$10^2\Delta_{AAD,\eta}$	0.8	4.3
$10^2\Delta_{Bias,\eta}$	−0.01	−0.3
$10^2\Delta_{MAD,\eta}$	1.8	13.5

The relatively poor performance of the Dymond−Assael model is not surprising considering that the mixture is highly asymmetric and very simple mixing rules were used that contain no adjustable parameters. We note that the mixture viscosity may be correlated along an individual isotherm using eqs 10, 11, and 13 with $\Delta_{AAD,\eta} \leq 12$ % when V_0 is treated as an adjustable parameter for each isotherm and composition. A quadratic mixing rule

$$V_0 = x_1^2 V_{0,1} + 2x_1x_2V_{0,12} + x_2^2 V_{0,2} \qquad (15)$$

was also investigated, where $V_{0,12}$ was given by

$$V_{0,12} = \frac{1}{2}\kappa(x_1V_{0,1} + x_2V_{0,2}) \qquad (16)$$

and κ is a binary parameter which we represented as a linear function of temperature

$$\kappa = \alpha + \beta\{(T/\mathrm{K}) - 300\} \qquad (17)$$

Optimization of the parameters in eq 17 yielded an improved representation of the mixture viscosity with $\Delta_{AAD,\eta} = 14$ %, $\Delta_{MAD,\eta} = 37$ %, $\alpha = 0.9739$, and $\beta = 5.06 \cdot 10^{-4}$. However, this is now a correlation rather than a prediction based upon the properties of the pure substances. In the temperature range investigated, we have $0.97 \leq \kappa \leq 1.05$, which indicates that the linear mixing rule for V_0 is not seriously in error.

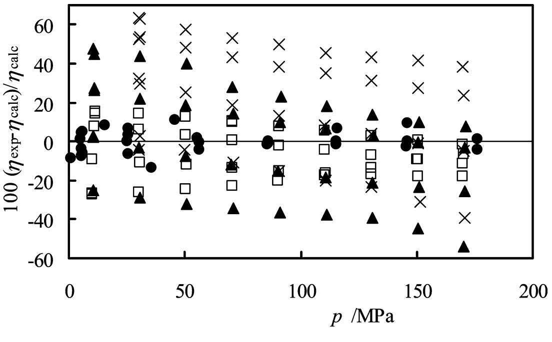

Figure 11. Deviations of experimental viscosities of CO_2 (1) + squalane (2) from the hard-sphere model: ●, $x_1 = 0$; □, $x_1 = 0.4233$; ▲, $x_1 = 0.6039$; ×, $x_1 = 0.7882$.

Conclusions

The viscosity and density of four different mixtures CO_2 (1) + squalane (2) were measured using a vibrating wire sensor. The results demonstrate that, over wide ranges of temperature and pressure, increasing the amount of CO_2 leads to a drastic decrement in the viscosity and a modest increment in the density. Empirical correlations have been developed which describe the viscosities and densities of each composition studied in terms of pressure and temperature; used with caution, these should also permit modest extrapolations to other state points. Interpolation may be used to estimate the properties at other compositions anywhere in the single-phase region bounded by $x_1 < 0.8$. The hard sphere model of Dymond and Assael, with linear mixing rules for the roughness factor and molar core volume, gives qualitatively correct predictions in terms of the dependence of viscosity upon temperature, pressure, and composition. However, in quantitative comparison with the experimental data, relative deviations of up to ± 60 % are found.

Literature Cited

(1) Lorentzen, G.; Pettersen, J. *Proceedings of IIR International Symposium*; Norway: Trondheim, 1992; pp 147−63.

(2) Marsh, K. N.; Kandil, M. E. Review of thermodynamic properties of refrigerants plus lubricant oils. *Fluid Phases Equilib.* **2002**, *199*, 319–334.

(3) Lugo, L.; Canet, X.; Comuñas, M. J. P.; Pensado, A. S.; Fernández, J. Dynamic viscosity under pressure for mixtures of Pentaerythritol ester lubricants with 32 viscosity grade: measurements and modeling. *Ind. Eng. Chem. Res.* **2007**, *46*, 1826–1835.

(4) Orr, F. M., Jr. *Theory of Gas Injection Processes*; Tie-Line Publication: Holte, Denmark, 2007.

(5) Stalkup, F. I. *Miscible Displacement*; Henry L. Doherty Series Monograph Vol. 8, Society of Petroleum Engineers of AIME: New York, 1983.

(6) Royal, D. D.; Vesovic, V.; Trusler, J. P. M.; Wakeham, W. A. Prediction of the viscosity of dense fluid mixtures. *Mol. Phys.* **2003**, *101*, 339–352.

(7) de Wijn, A. S.; Vesovic, V.; Jackson, G.; Trusler, J. P. M. A kinetic theory description of the viscosity of dense fluids consisting of chain molecules. *J. Chem. Phys.* **2008**, *128*, 204901.

(8) Liphard, K. G.; Schneider, G. M. Phase equilibria and critical phenomena in fluid mixtures of carbon dioxide + 2,6,10,15,19,23-hexamethyltetracosane up to 423 K and 100 MPa. *J. Chem. Thermodyn.* **1975**, *7*, 805–814.

(9) Sovovfi, H.; Khachaturyan, J. J. M. Solubility of squalane, dinonyl phthalate and glycerol in supercritical CO_2. *Fluid Phase Equilib.* **1997**, *137*, 185–191.

(10) Tomida, D.; Kumagai, A.; Yokoyama, C. Viscosity measurements and correlation of squalane + CO_2 mixture. *Int. J. Thermophys.* **2007**, *28*, 133–145.

(11) Pensado, A. S.; Comunas, M. J. P.; Lugo, L.; Fernández, J. High-pressure characterization of dynamic viscosity and derived properties for squalane and two Pentaerythritol ester lubricants: Pentaerythritol tetra-2-ethylhexanoate and Pentaerythritol tetranonanoate. *Ind. Eng. Chem. Res.* **2006**, *45*, 2394–2404.

(12) Bair, S. The high pressure rheology of some simple model hydrocarbons. *J. Eng. Tribol.* **2002**, *216*, 139–149.

(13) Bair, S. Reference liquids for quantitative elastohydrodynamics: selection and rheological characterization. *Tribol. Lett.* **2006**, *22*, 197–206.

(14) Krahn, U. G.; Luft, G. Viscosity of several liquid hydrocarbons in the temperature range 298 - 453 K at pressures up to 200 MPa. *J. Chem. Eng. Data* **1994**, *39*, 670–672.

(15) Fandino, O.; Pensado, A. S.; Lugo, L.; Comuñas, M. J. P.; Fernández, J. Compressed liquid densities of squalane and Pentaerythritol tetra(2-ethylhexanoate). *J. Chem. Eng. Data* **2005**, *50*, 939–946.

(16) Caudwell, D. R.; Vesovic, V.; Trusler, J. P. M.; Wakeham, W. A. The viscosity and density of n-dodecane and n-octadecane at pressures up to 200 MPa and temperatures up to 473 K. *Int. J. Thermophys.* **2004**, *25*, 1340–1352.

(17) Caudwell, D. Viscosity of Dense Fluid Mixture, PhD Thesis, University of London, 2004.

(18) Caudwell, D. R.; Trusler, J. P. M.; Vesovic, V.; Wakeham, W. A. Viscosity and Density of Five Hydrocarbon Liquids at Pressures up to 200 MPa and Temperatures up to 473 K. *J. Chem. Eng. Data* **2009**, *54*, 359−366.

(19) Retsina, T.; Richardson, S. M.; Wakeham, W. A. The theory of a vibrating-rod densimeter. *Appl. Sci. Res.* **1986**, *43*, 127–158.

(20) Retsina, T.; Richardson, S. M.; Wakeham, W. A. The theory of a vibrating-rod viscometer. *Appl. Sci. Res.* **1987**, *43*, 325–346.

(21) Dymond, J. H.; Øye, H. A. Viscosity of selected liquid normal alkanes. *J. Phys. Chem. Ref. Data* **1994**, *23*, 41–53.

(22) Huber, M. L.; Laesecke, A.; Xiang, H. W. Viscosity correlations for minor constituent fluids in natural gas: n-octane, n-nonane and n-decane. *Fluid Phase Equilib.* **2004**, *224*, 263–270.

(23) Span, R.; Wagner, W. Equations of State for Technical Applications. II. Results for Nonpolar Fluids. *Int. J. Thermophys.* **2003**, *24*, 41–109.

(24) Len, C. W.; Trusler, J. P. M.; Vesovic, V.; Wakeham, W. A. The viscosity of organic liquid mixtures. *Int. J. Thermophys.* **2006**, *27*, 48–65.

(25) Comuñas, M. J. P.; Baylaucq, A.; Boned, C.; Fernández, J. High pressure measurement of the viscosity and density of two polyethers and two dialkyl carbonates. *Int. J. Thermophys.* **2001**, *22*, 749–768.

(26) Dymond, J. H.; Malhotra, R. The Tait Equation: 100 Years On. *Int. J. Thermophys* **1988**, *9*, 941–951.

(27) Dymond, J. Transport properties in dense fluids, *Proc. 6th Symp. Thermophys. Prop.*; ASME: New York, 1973; pp 143−157.

(28) Assael, M. J.; Dymond, J. H.; Papadaki, M.; Patterson, P. M. Correlation and prediction of dense fluid transport coefficients. *Int. J. Thermophys* **1992**, *13*, 269–281.

(29) Vesovic, V.; Wakeham, W. A.; Olchowy, G. A.; Sengers, J. V.; Watson, J. T. R.; Millat, J. The transport properties of carbon dioxide. *J. Phys. Chem. Ref. Data* **1990**, *19*, 763–808.

(30) Span, R.; Wagner, W. A new equation of state for carbon dioxide covering the fluid region from the triple-point temperature to 1100 K at pressures up to 800 MPa. *J. Phys. Chem. Ref. Data* **1996**, *25*, 1509–1596.

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