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Liquid Viscosity and Density of Squalane and Squalane with Dissolved Carbon Dioxide at Temperatures From (298.15 to 548.15) K

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Abstract

The thermophysical properties of CO_2 + alkane mixtures involved in Fischer–Tropsch (FT) synthesis process are attracting attention. In this work, the viscosity and density of squalane and binary mixture of squalane with dissolved carbon dioxide were measured by using a vibrating-wire apparatus. The measurements were performed at temperatures from (298.15 to 548.15) K and pressures up to 10 MPa for squalane, and over the temperature range from (308.15 to 548.15) K and at pressures up to approximately 6 MPa for CO_2 + squalane under CO_2-saturated conditions. The estimated combined expanded uncertainties are 2.2% and 0.24% for viscosity and density, respectively, with a confidence level of 0.95 ($k=2$). The results show that the dissolution of CO_2 in squalane widens the density range and reduces greatly the viscosity when compared to pure squalane at the experimental temperature and pressure ranges. In addition, the experimental data of viscosity and density were correlated using the modified Tait-Andrade equation and Tait equation, respectively. The correlations developed in this work for both pure squalane and CO_2 + squalane mixture are in good agreement with the experimental results.

Keywords CO_2 · Density · Mixture · Squalene · Viscosity

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1 Introduction

The increasing environmental concerns and energy problems have drawn considerable attention to Fischer–Tropsch(FT) synthesis technology which converts synthesis gas ($CO + H_2$) from carbon feedstock such as natural gas, coal, biomass, etc. to synthetic hydrocarbon fuels and chemicals at an operation temperature from (448 to 623) K [1, 2]. The FT synthesis process generally involves complex products and reactants mixture systems of alkanes, olefins, alcohols, etc., and their mixtures with dissolved gases such as CO_2, CO, H_2, and N_2 [2]. The thermophysical properties of reactants and products involved in FT synthesis process, particularly at elevated temperatures, are crucial for the development and industrial scaling of the reactors. These properties, including viscosity, density, surface tension, etc., have a significant impact on the hydrodynamics of the reactors. Hydrodynamics determines the phase mixing, as well as the heat and mass transfer within the reactors [3]. Nonetheless, due to the complex mixed fluids involved in FT synthesis and extreme operational conditions, the research on thermophysical properties for relevant fluids is far from sufficient.

Our group has conducted studies on the thermophysical properties of pure and mixed fluids involved in FT synthesis. Yang et al. [4–6] utilized pendant drop method to measure the surface tension of alkanes, alcohols, alkane mixtures, and alkanes with dissolved CO_2 and N_2 at temperatures up to 573 K. Cui et al. [7, 8] utilized surface light scattering method to measure the viscosity of *n*-heptane or *n*-tetradecane with dissolved CO_2 at temperatures up to 473 K. Fu et al. [9, 10] and Liang et al. [11] used vibrating-wire method to measure the viscosity and density of alcohols, *n*-dodecane, and *n*-dodecane with dissolved CO_2 in a temperature range of (298 to 623) K and at pressures up to 10 MPa. Yang et al. [12] measured the viscosity and density of $CO_2 + n$-decane using a vibrating-wire viscometer coupled with a vibrating-tube densimeter at temperatures from (303 to 373) K and pressures up to 80 MPa.

Squalane plays a role in FT synthesis products and is a preferred option for modeling long-chain hydrocarbons. This particular branched alkane serves as a representative example of the paraffinic constituents in mineral oils. Despite the abundance of measured viscosity and density data of squalane in literature, experimental data for CO_2 + squalane are insufficient (Table 1). Tomida et al. [13] measured density and viscosity of CO_2 + squalane using a rolling ball viscometer and a glass piezometer, respectively, at four isotherms from (293.15 to 353.15) K, three pressures from (10.0 to 20) MPa, and at CO_2 mole fractions varied from 0 to 0.417; they have estimated the uncertainty of viscosity to be within 3%. Ciotta et al. [14] reported both density and viscosity using a vibrating-wire instrument at temperatures from (303.15 to 448.15) K and CO_2 mole fractions up to 0.788; they have performed the measurements at a very wide pressure range up to 171 MPa. Kandil et al. [15] also carried out density and viscosity measurements at temperatures between (313.15 to 363.15) K, pressures from slightly above bubble points up to about 75 MPa, and three CO_2 mole fractions of 0.199, 0.299, and 0.519 with a vibrating-tube densimeter and a capillary viscometer, respectively. Zambrano

Table 1 Summary of liquid viscosity and density for CO_2 + squalane in literature

Mixture	First author	Year	Method[a]	x_{CO2}[b]	T/K	p/MPa	Data points
Viscosity							
CO_2 + squalane	Tomida [13]	2007	RB	0.095–0.417	293–353	10–20	60
CO_2 + squalane	Ciotta [14]	2009	VW	0.4233–0.6039	303–448	10–171	116
CO_2 + squalane	Kandil [15]	2019	C	0.199–0.519	313–363	3–74	54
Density							
CO_2 + squalane	Tomida [13]	2007	P	0.095–0.417	293–353	10–20	60
CO_2 + squalane	Ciotta [14]	2009	VW	0.4233–0.6039	303–448	10–171	116
CO_2 + squalane	Zambrano [16]	2016	VTD	0.1001–0.2012	283–393	10–100	158
CO_2 + squalane	Kandil [15]	2019	VTD	0.199–0.519	313–363	3–74	54

[a] RB is rolling ball viscometer; VW is vibrating-wire viscometer; C is capillary; P is piezometer; VTD is vibrating-tube densimeter

[b] Mole fraction of CO_2

et al. [16] utilized an Anton Paar DMA HPM vibrating-tube densimeter to measure the density of CO_2 + squalane over a temperature range from (283.15 to 393.15) K, at pressures from (10 to 100) MPa and two CO_2 mole fractions of 0.1001 and 0.2012. Although the viscosity and density of CO_2 + squalane were measured up to a high pressure of 171 MPa, all the available data are for sub-saturated mixtures of CO_2 in squalane and below 448 K, which is inadequate for the development of high-precision density and viscosity models for CO_2 + squalane, particularly at high temperatures.

This work describes continuing work on the thermophysical properties of alkanes and alkanes with dissolved CO_2 involved in FT synthesis. The viscosity and density measurements of squalane and CO_2 + squalane were conducted by using a vibrating-wire apparatus. The measurements were carried out at eleven isotherms from (298.15 to 548.15) K and six pressures starting at 0.1 MPa up to 10 MPa for squalane and at eleven isotherms from (308.15.15 to 548.15) K and five pressures approximately ranging from (1 to 6) MPa for CO_2 + squalane. The experimental data would serve as a foundational basis for future modeling studies on CO_2 + alkane mixed fluids. Furthermore, the experimental viscosity and density data were correlated using the modified Tait-Andrade equation and Tait equation, respectively. The comparisons of correlations with the available literature data were discussed for squalene.

2 Experimental

2.1 Materials

Table 2 presents the information on chemical materials used in this work. CO_2 was provided by Shaanxi Yulong Gas with a declared mass purity higher than 0.99999.

Table 2 Specification of Chemical Materials

Chemical name	Molecular formula	CASRN	Source	Mass purity[a]
Carbon dioxide	CO_2	124-38-9	Shaanxi Yulong Gas	>0.99999
Squalane	$C_{30}H_{62}$	111-01-3	Acros Organics	>0.99

[a] Provide by suppliers without further purification and purity measurements

Squalane was supplied by Acros Organics with a declared mass purity higher than 0.99.

2.2 Apparatus

The experimental measurements of squalane and CO_2 + squalane were carried out by using a vibrating-wire apparatus described recently [11]. The apparatus employed a centerless-ground tungsten wire with a nominal radius of 0.05 mm and a nominal length of 50 mm. The wire was inserted vertically between two permanent magnets made of Sm2Co17 that can be operated at a maximum temperature of 623 K. To achieve viscosity and density measurements simultaneously, the upper end of the wire was clamped in a fixed support, while the lower end was tensioned by a sinker made of aluminum alloy 6061 and with a mass of 226.91 g. The wire, magnets, and sinker were assembled in the middle of a stainless steel high-pressure vessel by a supporting structure. During the experiment, the wire was submerged by the investigated fluid, and driven by a constant sinusoidal current to operate transverse vibration. The electromotive force in the vicinity of the fundamental transverse resonance frequency developed across the wire was detected as a function of frequency by a lock-in amplifier (model 7230, AMETEK). If all the other necessary parameters in the working equation were given, the viscosity and density of the studied fluid were obtained through a nonlinear optimization process that minimized the deviation between the experimental data and the working equation.

The temperature of the vibrating-wire apparatus was measured by a temperature measurement instrument connected with a platinum resistance thermometer which was calibrated before use. The combined expanded uncertainty of temperature measurements is estimated to be $U_c(T) = 25$ mK with a level of confidence of 0.95 ($k = 2$). For pure liquids sample and their mixtures measurements, the pressure of the experimental apparatus was regulated by a piston screw pump. For gas-saturated alkane measurements, the pressure was adjusted mainly by a high-pressure gas regulator combined with an air compressor. The pressure of the experimental apparatus was measured in external pipework using a Druck UNIK 5000 pressure transducer which has an accuracy of 0.1% for the full-scale range from (0 to 15) MPa. The output signal of the pressure transducer was read by an Agilent 34970A. The combined expanded uncertainty of the measured pressure is $U_c(p) = 18$ kPa ($k = 2$).

To ensure precise density measurement at elevated temperatures, we utilized a refined expression for f_0, which is the “buoyancy-corrected” fundamental transverse resonance frequency of the wire in vacuum. This refined expression was initially presented by Ciotta and Trusler [17]. Additionally, we introduced a temperature-dependent function for the linear thermal expansion coefficient of the sinker [11]. Prior to conducting experimental measurements of the studied samples, the calibration measurements were carried out in vacuum and with toluene. In addition, validation measurements were performed with toluene at temperatures from (298 to 548) K and pressures up to 10 MPa. More details were presented in our recently published work [11]. Furthermore, we followed the same methodology as our previous work [6] to analyze the measurement uncertainty of the vibrating-wire apparatus [9]. The combined expanded uncertainties are estimated to be 2.2% for viscosity and 0.24% for density with a confidence level of 0.95 ($k=2$).

3 Results

Measurements at every experimental condition were repeated more than three times and the mean of multiple repeated measurements was ascribed to be the experimental results. Table 3 displays the measured viscosities and densities of squalane. The experimental data were obtained at 11 isotherms spanning temperatures from (298.15 to 548.15) K and pressures from (0.1 to 10) MPa.

Table 4 illustrates the experimental viscosities and densities of CO_2 + squalane. The measurements were conducted at CO_2-saturated conditions across 11 isotherms ranging from (308.15 to 548.15) K and at pressures from (1 to 6) MPa. After the measurement of CO_2 + squalane at 548.15 K, 2.37 MPa, the apparatus was cooled down naturally, and then the viscosity and density were remeasured at 348.15 K, 1.13 MPa. The remeasurement results are in good agreement with the initial measurements, with deviations of less than 0.6% for viscosity and 0.12% for density. In order to further verify the reliability of the experimental results, after the experiment of 548.15 K, 5.67 MPa, the apparatus was cooled down to the atmospheric temperature naturally. The sample was then discharged, and the apparatus was cleaned and vacuumed. A new squalane sample was introduced for subsequent remeasurements of viscosity and density. The remeasurements were taken at the following conditions: 498.15 K, 2.35 MPa/3.55 MPa/5.65 MPa; 523.15 K, 1.29 MPa/2.36 MPa/3.59 MPa; 548.15 K, 1.30 MPa/2.37 MPa/3.59 MPa. The remeasurement results were compared with the first measured results, showing deviations of less than 0.19% for viscosity and 0.16% for density. All the measurements indicate that the sample dose not deteriorate after the high-temperature experiment and the experimental results are stable and reliable. Our group has conducted measurements of the solubility of CO_2 + squalane at temperatures ranging from (300 to 523) K and at pressures up to 10 MPa, and developed solubility predictive models by the volume-translated Peng–Robinson equation of state (VTPR) in combination with van der Waals mixing rules [6]. The mole fractions of CO_2 (x_{CO2}) calculated by solubility predictive models are also listed in Table 4. The combined expanded uncertainty of the calculated x_{CO2} is estimated to be 3.5% ($k=2$).

Figures 1 and 2 demonstrate the viscosities and densities of squalane as a function of pressure, respectively. The trends for both viscosities and densities show a close-to-linear increase with increasing pressure, while they decrease as temperature

Table 3 Viscosities η and densities ρ of squalane measured with a vibrating-wire apparatus at temperatures T from (298.15 to 548.15) K and pressures p up to 10 MPa[a]

T/K	p/MPa	ρ/kg·m^{-3}	η/mPa·s	T/K	p/MPa	ρ/kg·m^{-3}	η/mPa·s
298.15	0.10	805.29	27.774	423.15	6.00	732.33	1.617
298.15	2.00	806.38	28.997	423.15	8.00	734.38	1.665
298.15	4.00	807.58	30.330	423.15	10.00	736.35	1.716
298.15	6.00	809.03	31.692	448.15	0.10	709.24	1.103
298.15	8.00	810.37	33.028	448.15	2.00	711.61	1.138
298.15	10.00	811.56	34.567	448.15	4.00	714.03	1.173
323.15	0.10	789.57	10.554	448.15	6.00	716.42	1.209
323.15	2.00	790.75	10.991	448.15	8.00	718.69	1.245
323.15	4.00	792.61	11.386	448.15	10.00	720.9	1.282
323.15	6.00	794.29	11.798	473.15	0.10	692.16	0.853
323.15	8.00	795.78	12.213	473.15	2.00	694.88	0.883
323.15	10.00	797.56	12.618	473.15	4.00	697.74	0.912
348.15	0.10	773.92	5.268	473.15	6.00	700.38	0.941
348.15	2.00	775.56	5.461	473.15	8.00	702.92	0.971
348.15	4.00	777.38	5.657	473.15	10.00	705.4	1.001
348.15	6.00	778.84	5.861	498.15	0.10	674.92	0.685
348.15	8.00	780.47	6.067	498.15	2.00	678.14	0.709
348.15	10.00	781.94	6.274	498.15	4.00	681.35	0.734
373.15	0.10	758.67	3.130	498.15	6.00	684.51	0.756
373.15	2.00	760.46	3.231	498.15	8.00	687.53	0.780
373.15	4.00	762.24	3.341	498.15	10.00	690.31	0.804
373.15	6.00	764.02	3.445	523.15	0.10	657.85	0.556
373.15	8.00	765.74	3.560	523.15	2.00	661.58	0.576
373.15	10.00	767.34	3.672	523.15	4.00	665.22	0.598
398.15	0.10	742.91	2.073	523.15	6.00	668.66	0.620
398.15	2.00	744.76	2.138	523.15	8.00	671.95	0.642
398.15	4.00	746.71	2.204	523.15	10.00	675.08	0.663
398.15	6.00	748.59	2.274	548.15	0.10	639.89	0.466
398.15	8.00	750.43	2.341	548.15	2.00	644.19	0.485
398.15	10.00	752.17	2.413	548.15	4.00	648.35	0.505
423.15	0.10	726.04	1.472	548.15	6.00	652.35	0.523
423.15	2.00	728.13	1.518	548.15	8.00	656.08	0.542
423.15	4.00	730.22	1.569	548.15	10.00	659.66	0.559

[a] The combined expanded uncertainties $U_c(k=2)$ are $U_c(T)=25$ mK, $U_c(p)=18$ kPa, $U_c(\rho)=0.0024\rho$, $U_c(\eta)=0.022\eta$ with a confidence level of 0.95

increases. At lower temperatures, the viscosities exhibit a rapid decrease with increasing temperature, while at higher temperatures the decrease is more gradual.

The relationship between pressure and the viscosities of CO_2 + squalane is illustrated in Fig. 3. At low temperatures, the viscosities present a considerable decrease with increasing pressure as the increase of CO_2 solubility in liquid squalane, while at

Table 4 Viscosities η and densities ρ of CO_2 + squalane measured with a vibrating-wire apparatus at temperatures T from (308.15 to 548.15) K and pressures p up to 6 MPa[a]

T/K	p/MPa	x_{CO2}[b]	ρ/kg·m^{-3}	η/mPa·s	T/K	p/MPa	x_{CO2}[b]	ρ/kg·m^{-3}	η/mPa·s
308.15	1.10	0.183	802.32	12.946	448.15	4.44	0.292	710.35	0.896
308.15	2.04	0.319	805.76	8.916	448.15	5.56	0.352	710.81	0.855
308.15	3.05	0.446	809.55	6.662	473.15	1.25	0.086	692.16	0.814
308.15	4.04	0.555	814.22	5.077	473.15	2.35	0.155	692.48	0.780
308.15	5.07	0.652	815.82	3.940	473.15	3.48	0.221	692.85	0.747
323.15	1.10	0.159	791.67	8.019	473.15	4.45	0.274	693.01	0.718
323.15	2.09	0.284	794.90	6.410	473.15	5.58	0.331	693.42	0.689
323.15	3.16	0.402	797.89	5.162	498.15	1.28	0.081	674.69	0.654
323.15	4.14	0.498	800.14	4.216	498.15	2.36	0.146	674.63	0.630
323.15	5.21	0.588	801.96	3.418	498.15	3.50	0.209	675.85	0.606
348.15	1.14	0.135	775.28	4.416	498.15	4.47	0.259	675.15	0.587
348.15	2.18	0.245	777.63	3.824	498.15	5.60	0.313	676.21	0.565
348.15	3.29	0.347	779.58	3.294	523.15	1.28	0.078	657.52	0.535
348.15	4.27	0.429	781.05	2.885	523.15	2.37	0.139	656.90	0.518
348.15	5.35	0.508	784.92	2.517	523.15	3.51	0.199	658.29	0.499
373.15	1.19	0.121	758.83	2.765	523.15	4.49	0.246	657.19	0.485
373.15	2.24	0.216	759.95	2.485	523.15	5.66	0.298	657.12	0.469
373.15	3.34	0.306	761.30	2.240	548.15	1.28	0.077	639.67	0.444
373.15	4.35	0.380	762.81	2.040	548.15	2.38	0.138	638.82	0.431
373.15	5.38	0.449	763.33	1.864	548.15	3.52	0.198	640.26	0.417
398.15	1.22	0.109	742.34	1.882	548.15	4.51	0.246	638.80	0.406
398.15	2.29	0.195	743.04	1.738	548.15	5.67	0.300	638.52	0.393
398.15	3.40	0.277	744.45	1.607	348.15	1.13	0.134	776.21	4.444
398.15	4.38	0.343	745.23	1.500	498.15	2.35	0.145	674.62	0.631
398.15	5.49	0.411	746.96	1.396	498.15	3.55	0.211	675.43	0.605
423.15	1.24	0.100	725.94	1.364	498.15	5.65	0.315	675.10	0.564
423.15	2.32	0.179	726.16	1.282	523.15	1.29	0.078	657.38	0.535
423.15	3.45	0.255	727.30	1.207	523.15	2.36	0.138	656.92	0.518
423.15	4.41	0.315	727.68	1.143	523.15	3.57	0.201	657.90	0.499
423.15	5.50	0.377	728.86	1.099	548.15	1.30	0.075	639.72	0.444
448.15	1.25	0.092	709.12	1.036	548.15	2.37	0.133	638.86	0.431
448.15	2.34	0.166	709.56	0.987	548.15	3.59	0.193	639.91	0.416
448.15	3.48	0.237	709.94	0.937					

[a] The combined expanded uncertainties $U_c(k=2)$ are $U_c(T) = 25$ mK, $U_c(p) = 18$ kPa, $U_c(x_{CO2}) = 0.035x_{CO2}$, $U_c(\rho) = 0.0024\rho$, $U_c(\eta) = 0.022\eta$ with a confidence level of 0.95

[b] Mole fractions of CO_2 are calculated with the solubility prediction model proposed by our group [6]

higher temperatures, the decrease in viscosity with increasing pressure is relatively slower. Figure 4 presents the pressure-dependant densities of CO_2 + squalane. Along the isotherms, for temperatures below 498.15 K, the densities of CO_2 + squalane increase with increasing pressure (or x_{CO2}), while for temperatures above 523.15 K,

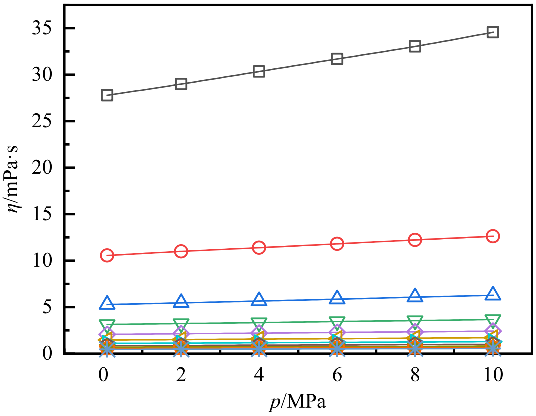


Fig. 1 Viscosities of squalane as a function of pressure: □, 298.15 K; ○, 323.15 K; △, 348.15 K; ▽, 373.15 K; ◇, 398.15 K; ◁ 423.15 K; ▷, 448.15 K; ⬡, 473.15 K; ☆, 498.15 K; ⬠, 523.15 K; ✳, 548.15 K

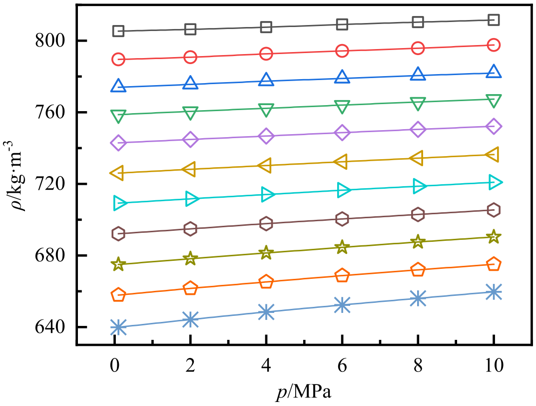


Fig. 2 Densities of squalane as a function of pressure:□, 298.15 K; ○, 323.15 K; △, 348.15 K; ▽, 373.15 K; ◇, 398.15 K; ◁, 423.15 K; ▷, 448.15 K; ⬡, 473.15 K; ☆, 498.15 K; ⬠, 523.15 K; ✳, 548.15 K

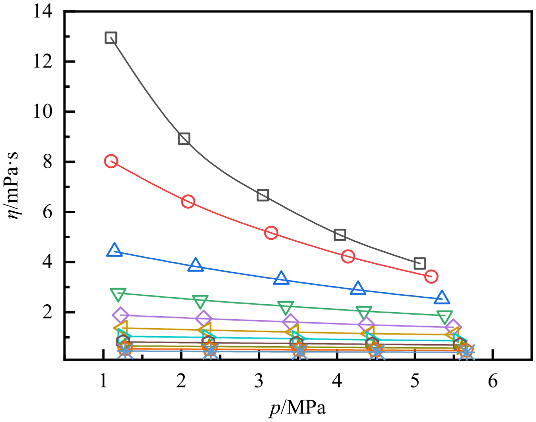


Fig. 3 Viscosities of CO_2 + squalane as a function of pressure: □, 308.15 K; ○, 323.15 K; △, 348.15 K; ▽, 373.15 K; ◇, 398.15 K; ◁, 423.15 K; ▷, 448.15 K; ⬡, 473.15 K; ☆, 498.15 K; ⬠, 523.15 K; ✳, 548.15 K

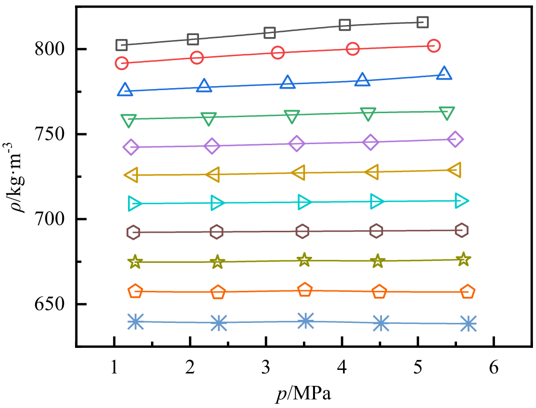


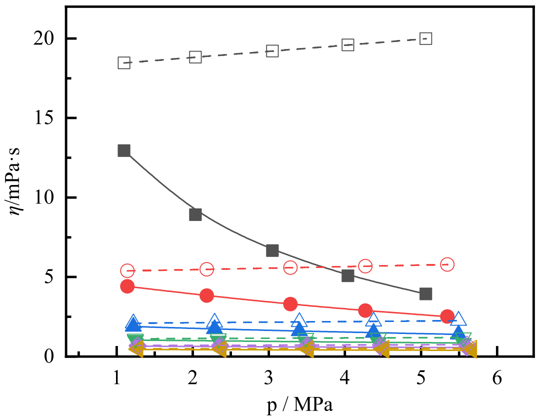
Fig. 4 Densities of CO_2 + squalane as a function of pressure: □, 308.15 K; ○, 323.15 K; △, 348.15 K; ▽, 373.15 K; ◇, 398.15 K; ◁, 423.15 K; ▷, 448.15 K; ⬡, 473.15 K; ☆, 498.15 K; ⬠, 523.15 K; ✳, 548.15 K

an opposing trend occurs where densities decrease with increasing pressure (or x_{CO2}), but the decrease is accompanied by noticeable fluctuations and the downward trend is not very pronounced. The possible reason is that the decrease of density with the increase of pressure is smaller than the density measurement uncertainty of the vibrating-wire apparatus used at 523.15 K and 548.15 K. Along the isobars, densities decrease with increasing temperature.

Figure 5 depicts a comparison of viscosities between squalane and CO_2 + squalane at temperatures from (308.15 to 548.15) K. At the same temperature and pressure of CO_2 + squalane, the viscosities of squalane were calculated from Eq. 1 described in Sect. 4. It is apparent that the viscosities of CO_2 + squalane are always lower than that of squalane at the same temperature and pressure. In addition, the viscosities of squalane increase slightly with increasing pressures, while viscosities of CO_2 + squalane decrease significantly with increasing pressures. For example, at a temperature of 308.15 K and a pressure of 1.10 MPa, the viscosity of pure squalane is about 1.4 times as much as CO_2 + squalane. However, at a higher pressure of 5.07 MPa and the same temperature of 308.15 K, the viscosity difference is significantly greater, the viscosity of pure squalane is about 5.1 times as much as CO_2 + squalane. This substantial variation is mainly due to the increased concentration of CO_2 in liquid squalane, rather than the rise in pressure.

Figure 6 shows the density comparisons between squalane and CO_2 + squalane over a temperature range of (308.15 to 548.15) K. Densities of squalane were calculated from Eq. 5 described in Sect. 4 at the same condition of CO_2 + squalane. It is evident that at low temperatures (e.g., 308.15 K, 348.15 K), the densities of CO_2 + squalane are greater than that of squalane due to the influence of CO_2. However, at a temperature of 398.15 K, the densities of CO_2 + squalane are nearly identical to that of pure squalane. As the temperature rises further (e.g., 448.15 K, 498.15 K, 548.15 K), CO_2 dissolves into pure squalane resulting in a decrease in density. Therefore, the dissolution of CO_2 widens the density range of CO_2 + squalane when compared to pure squalane.

Fig. 5 Comparison of the viscosities between squalane and CO_2 + squalane at temperatures from (308.15 to 548.15) K. Hollow dots (squalane): □, 308.15 K; ○, 348.15 K; △, 398.15 K; ▽, 448.15 K; ◇, 498.15 K; ◁, 548.15 K. Solid dots (CO_2 + squalane): ■, 308.15 K; ●, 348.15 K; ▲, 398.15 K; ▼, 448.15 K; ◆, 498.15 K; ◀, 548.15 K



4 Correlations

4.1 Correlations for Squalane

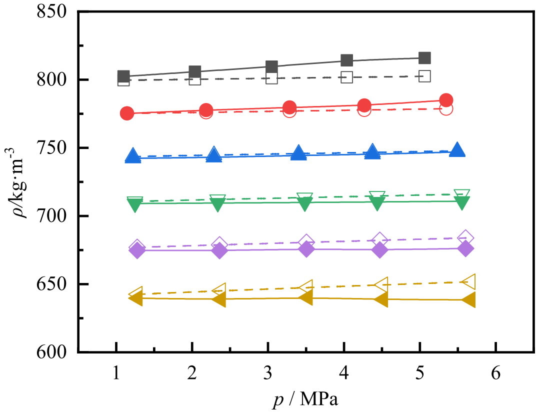
To correlate the viscosity data of squalane, the modified Tait-Andrade equation [11] was used:

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

where, $p_0 = 0.1$ MPa; A_η and C_η are constants; B_η is a cubic function of reduced temperature; D and E are quadratic functions of reduced temperature.

$$B_\eta = \sum_{i=0}^{3} b_{\eta,i}\left(T/T_0\right)^i \tag{2}$$

Fig. 6 Comparison of the densities between squalane and CO_2 + squalane at temperatures from (308.15 to 548.15) K. Hollow dots (squalane): □, 308.15 K; ○, 348.15 K; △, 398.15 K; ▽, 448.15 K; ◇, 498.15 K; ◁, 548.15 K. Solid dots (CO_2 + squalane): ■, 308.15 K; ●, 348.15 K; ▲, 398.15 K; ▼, 448.15 K; ◆, 498.15 K; ◀, 548.15 K



$$D = \sum_{i=0}^{2} d_i \left(T/T_0\right)^{-i} \tag{3}$$

$$E = \sum_{i=0}^{2} e_i \left(T/T_0\right)^{i} \tag{4}$$

where, $T_0 = 298.15$ K; $b_{\eta,\mathrm{i}}$, d_i, and e_i are adjusted coefficients by fitting to the measured viscosity data.

A modified Tait equation [11] was used to correlate the density data of squalane

$$\rho = \rho_0 \left[1 - C \ln\left(\frac{p + B}{p_0 + B}\right)\right]^{-1} \tag{5}$$

where, $p_0 = 0.1$ MPa; ρ_0 is the density at $p = p_0$; C is a constant. ρ_0 and B are cubic functions of reduced temperature as follows:

$$\rho_0 = \sum_{i=0}^{3} a_i \left(T/T_0\right)^{i} \tag{6}$$

$$B = \sum_{i=0}^{3} b_i \left(T/T_0\right)^{i} \tag{7}$$

in which, a_i and b_i are determined by fitting to the experimental densities.

For further analysis, the statistical values of fitting, the average absolute relative deviations (AAD), the maximum absolute relative deviations (MAD), and the average relative bias (Bias) were defined as follows:

$$\mathrm{AAD}/\% = \frac{100}{N} \sum_{i=1}^{i=N} \left| \frac{X_{i,\mathrm{exp}} - X_{i,\mathrm{cal}}}{X_{i,\mathrm{cal}}} \right| \tag{8}$$

$$\mathrm{MAD}/\% = 100 \cdot \max\left(\left| \frac{X_{i,\mathrm{exp}} - X_{i,\mathrm{cal}}}{X_{i,\mathrm{cal}}} \right| \right) \tag{9}$$

$$\mathrm{Bias} \,/\, \% = \frac{100}{N} \sum_{i=1}^{i=N} \left(\frac{X_{i,\mathrm{exp}} - X_{i,\mathrm{cal}}}{X_{i,\mathrm{cal}}} \right) \tag{10}$$

Table 5 presents the coefficients obtained from viscosity and density correlations for squalane, respectively. The AADs of viscosity and density are 0.37% and 0.02%, respectively, indicating that the correlations are accurate in describing the experimental data in this work.

The viscosity and density comparisons between experimental data and the correlations were made at experimental conditions of this work. The viscosity deviations

Table 5 Coefficients of modified Tait-Andrade equation and Tait equation and for squalane

Modified Tait-Andrade equation		Modified Tait equation	
Coefficients	Values	Coefficients	Values
A_η	1.04928×10^{-1}	a_0	9.42327×10^{2}
C_η	-1.77490×10^{2}	a_1	-9.10342×10^{1}
$b_{\eta,0}$	5.99517×10^{2}	a_2	-5.44090×10^{1}
$b_{\eta,1}$	1.03939×10^{2}	a_3	7.87145
$b_{\eta,2}$	1.48885×10^{1}	b_0	6.95235×10^{1}
$b_{\eta,3}$	-4.52172×10^{1}	b_1	1.74929×10^{2}
d_0	5.66638×10^{1}	b_2	-2.07248×10^{2}
d_1	-1.00393×10^{2}	b_3	5.34501×10^{1}
d_2	4.71003×10^{1}	C	8.31141×10^{-2}
e_0	-4.58422×10^{2}	AAD/%	0.02
e_1	3.25067×10^{2}	MAD/%	0.07
e_2	2.81641×10^{2}	Bias/%	0.00
AAD/%	0.37		
MAD/%	2.10		
Bias/%	– 0.02		

are demonstrated in Fig. 7. Except for several points where the deviation is large, the viscosity deviations are generally within ± 3%. The largest deviation is the viscosity at 353.15 K, 0.1 MPa measured by Krahn and Luft [18] using a rolling ball viscometer, with a deviation of 7.33%. In addition, the viscosity at 313.15 K, 10 MPa measured by Comunas et al. [19] shows a large negative deviation of -6.86%. The density deviations are almost within ± 0.3% as shown in Fig. 8. The data point with the

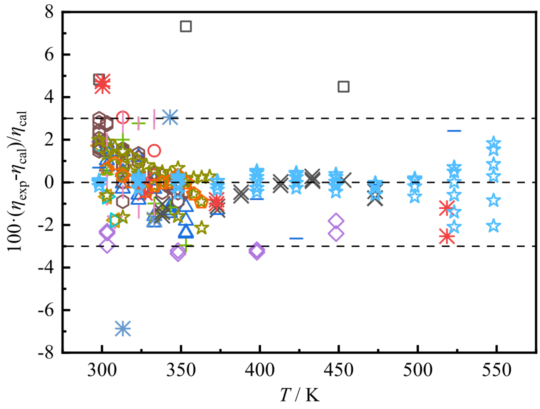


Fig. 7 Squalane viscosity deviations as a function of temperature between experiment and correlation. ☆, This work; □, Krahn and Luft [18]; ○, Kumagai et al. [22]; △, Pensado et al. [23]; ▽, Dubey and Sharma [24]; ◇, Ciotta et al. [14]; ◁, Dubey et al. [25]; ▷, Dubey et al. [26]; ⬡, Harris [27]; ☆, Comuñas et al. [28]; ⬠, Mylona et al. [29]; ✳, Comuñas et al. [19]; +, Gaciño et al. [30]; ×, Schmidt et al. [21]; ✳, Rowane et al. [20]; —, Klein et al. [31]; |, Bürk et al. [32]

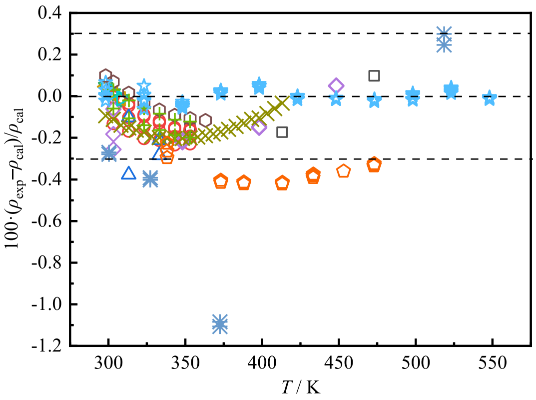


Fig. 8 Squalane density deviations as a function of temperature between experiment and correlation. ☆, This work; □, Korosi and Kováts [33]; ○, Fandiño et al., [34]; △, Kumagai et al. [22]; ▽, Dubey and Sharma [24]; ◇, Ciotta et al., [14]; ◁, Dubey et al. [25]; ▷, Dubey et al. [26]; ⬡, Harris [27]; ×, Korotkovskii et al. [35]; ⬠, Schmidt et al. [21]; ✳, Rowane et al. [20]; +, Bürk et al. [32]

maximum deviation was measured by Rowane et al. [20] using a rolling ball densitometer/viscometer at 372.6 K, 4 MPa, with a deviation of – 1.11%. Additionally, the density data reported by Schmidt et al. [21] utilizing the vibrating-wire method demonstrate an overall negative deviation ranging from (– 0.42 to – 0.26) %.

4.2 Correlations for CO_2 + Squalane

Utilizing the viscosity data of binary mixtures composed of methane and carbon dioxide with hydrocarbons up to *n*-hexadecane, Thol and Richter [36] conducted an analysis of the extended corresponding states method, two different entropy scaling approaches, and the friction theory regarding their efficacy in predicting viscosity with increasing asymmetry of the binary mixtures. According to their analysis, the precise prediction of viscosity for asymmetry mixtures remains a challenge primarily due to limited experimental data and the significant influence of high asymmetry. Similarly, the accurate density modeling of asymmetry mixtures also presents significant difficulty. Tait-like equations were most commonly used to correlate the viscosities and densities of CO_2 + alkane mixtures at every single composition [14, 16, 37]. While the correlations may not accurately extrapolate to other state points, they closely match the experimental data when used for interpolation.

Experimental viscosity and density data of CO_2 + squalane were fitted to the modified Tait-Andrade equation and Tait equation mentioned above, respectively. According to Binti Mohd Taib [38], parameters in the equations could be expressed as functions of the mole fraction of CO_2, x:

$$A_\eta = A_{\eta,0} + A_{\eta,1}x \tag{11}$$

$$B_\eta = B_{\eta,0} + B_{\eta,1}x \tag{12}$$

$$C_\eta = C_{\eta,0} + C_{\eta,1}x \tag{13}$$

$$D = \sum_{i=0}^{2} \left(d_{i,0} + d_{i,1}x\right)\left(T/T_0\right)^{-i} \tag{14}$$

$$E = \sum_{i=0}^{2} \left(e_{i,0} + e_{i,1}x\right)\left(T/T_0\right)^{i} \tag{15}$$

$$\rho_0 = \sum_{i=0}^{2} \left(a_{i,0} + a_{i,1}x\right)\left(T/T_0\right)^{i} \tag{16}$$

$$B = \sum_{i=0}^{2} \left(b_{i,0} + b_{i,1}x\right)\left(T/T_0\right)^{i} \tag{17}$$

$$C = c_0 + \mathrm{c}_1 x \tag{18}$$

Coefficients of viscosity and density correlations for CO_2 + squalane are presented in Table 6. The AADs for viscosity and density are 0.65% and 0.04%, respectively, indicating that the correlations are able to accurately reproduce our measured data.

The deviations between the experimental data and calculated values from correlations for viscosity and density are shown in Figs. 9 and 10, respectively. The viscosity deviations are generally within 0.1%, and the density deviations are almost within 0.1%. These deviations are evenly distributed on both sides of the zero line, except for the viscosity deviations at the maximum temperature of 548.15 K. As can be seen from Fig. 9, the viscosity deviation absolute values increase with the increasing pressure reaching 4.67% at 5.67 MPa. The possible reason for the large deviations is that the viscosity value changes sharply from the experimental temperature of 308.15 K to 548.15 K, from 12.946 mPa·s to 0.393 mPa·s. The modified Tait-Andrade equation adopted in this section may not be able to describe such a drastic change in viscosity very accurately.

5 Conclusions

In this work, viscosity and density measurements of squalane and CO_2 + squalane were conducted using a vibrating-wire apparatus up to high temperatures of 548.15 K. The experimental data were fitted by the modified Tait equation for density data and the modified Tait-Andrade equation for viscosity data, respectively. The developed empirical correlations of pure squalane and CO_2 + squalane binary mixtures are able to represent the measured data of this work almost within experimental uncertainties. By comparing the squalane viscosity and density correlations with existing literature data, it was found that the viscosity and density deviations were largely within 0.3% and 3%, respectively. The viscosity

Table 6 Coefficients of modified Tait-Andrade equation and Tait equation for CO_2 + squalane

Modified Tait-Andrade equation		Modified Tait equation	
Coefficients	Values	Coefficients	Values
$A_{\eta,0}$	3.50673	$a_{0,0}$	9.55868×10^{2}
$A_{\eta,1}$	5.99318×10^{-1}	$a_{0,1}$	1.43628×10^{2}
$B_{\eta,0}$	5.44153×10^{1}	$a_{1,0}$	-1.30231×10^{2}
$B_{\eta,1}$	6.22782×10^{2}	$a_{1,1}$	-1.57068×10^{2}
$C_{\eta,0}$	-1.75297×10^{2}	$a_{2,0}$	-2.28677×10^{1}
$C_{\eta,1}$	1.76441×10^{1}	$a_{2,1}$	4.38825×10^{1}
$d_{0,0}$	-7.00704×10^{-1}	$b_{0,0}$	6.64986×10^{4}
$d_{0,1}$	9.18192×10^{-2}	$b_{0,1}$	-5.96889×10^{4}
$d_{1,0}$	3.25828×10^{-1}	$b_{1,0}$	-4.84799×10^{4}
$d_{1,1}$	-2.53165×10^{-1}	$b_{1,1}$	1.19037×10^{-1}
$d_{2,0}$	5.94215×10^{-1}	$b_{2,0}$	7.75965×10^{3}
$d_{2,1}$	-8.21030×10^{-1}	$b_{2,1}$	1.42084×10^{4}
$e_{0,0}$	-1.12177×10^{-1}	c_0	-9.89218×10^{-2}
$e_{0,1}$	-5.23073×10^{-2}	c_1	1.71628×10^{-1}
$e_{1,0}$	1.58876×10^{-2}	AAD/%	0.04
$e_{1,1}$	7.37631×10^{-2}	MAD/%	0.14
$e_{2,0}$	-5.07656×10^{-3}	Bias/%	0.00
$e_{2,1}$	-1.63545×10^{-2}		
AAD/%	0.65		
MAD/%	4.67		
Bias/%	– 0.07		

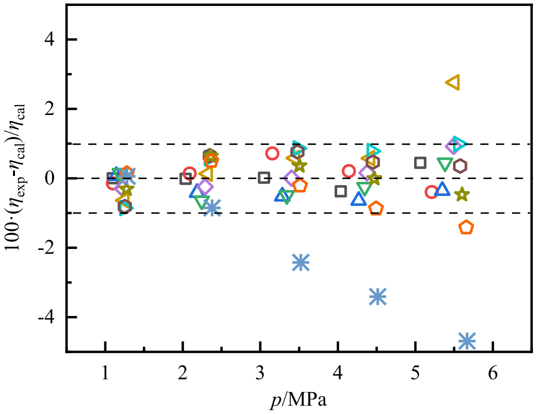
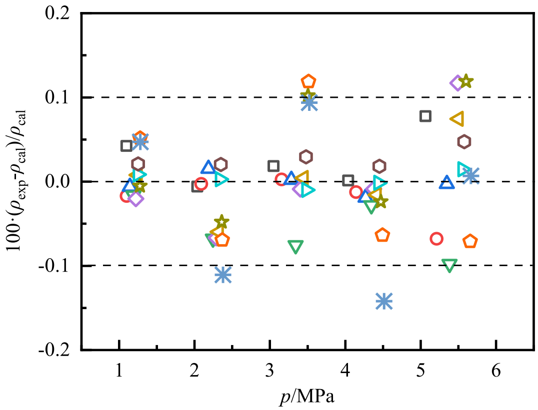


Fig. 9 CO_2 + squalane viscosity deviations between experiment and correlation. □, 308.15 K; ○, 323.15 K; △, 348.15 K; ▽, 373.15 K; ◇, 398.15 K; ◁, 423.15 K; ▷, 448.15 K; ⬡, 473.15 K; ☆, 498.15 K; ⬠, 523.15 K; ✳, 548.15 K

and density of CO_2-saturated squalane were first measured. The experimental data obtained in this work can fill in the gaps in experimental viscosity and density data of CO_2 + squalane systems under CO_2-saturated conditions and at

Fig. 10 CO_2 + squalane density deviations between experiment and correlation. □, 308.15 K; ○, 323.15 K; △, 348.15 K; ▽, 373.15 K; ◇, 398.15 K; ◁, 423.15 K; ▷, 448.15 K; ⬡, 473.15 K; ☆, 498.15 K; ⬠, 523.15 K; ✳, 548.15 K



high-temperature regions. Furthermore, these data can serve as a fundamental basis for theoretical and empirical modeling, as well as molecular simulations.

Author Contributions XL conducted experimental measurements and wrote the main manuscript text. XM and JW proposed the research content and made modifications to the manuscript. JY contributed to experimental data analysis and made modifications. XZ contributed to experimental measurements. All authors reviewed the manuscript.

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Data Availability The data are available from the corresponding author upon reasonable request.

Declarations

Competing interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Ethical Approval Not applicable.

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