

**Reference Correlations for the Density and Viscosity of Squalane
from 273 to 473 K at pressures to 200 MPa**

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This paper presents new reference correlations for both the density and viscosity of squalane at high pressure. These correlations are based on critically evaluated experimental data taken from the literature. In the case of the density, the correlation, based on the Tait equation, is valid from 273 to 473 K at pressures to 200 MPa. At 0.1 MPa, it has an average absolute deviation of 0.03%, a bias of -0.01%, and an expanded uncertainty (at the 95% confidence level) of 0.06%. Over the whole range of pressures, the density correlation has an average absolute deviation of 0.05%, a bias of -0.004%, and an expanded uncertainty (at the 95% confidence level) of 0.18%.

In the case of the viscosity, two correlations are presented, one a function of density and temperature, based on the Assael-Dymond model, and the other a function of temperature and pressure, based on a modified Vogel-Fulcher-Tammann equation. The former is slightly superior to the latter at high temperatures (above 410 K), whereas the reverse is true at low temperatures, where the viscosity is strongly temperature dependent. In the temperature range from 320 to 473 K at pressures to 200 MPa, the first correlation has an average absolute deviation of 1.41%, a bias of -0.09%, and an expanded uncertainty (at the 95% confidence level) of 3%. Below 320 K, deviations from the present scheme rise to a maximum of 20%. In the temperature range from 278 to 473 K at pressures to 200 MPa the second viscosity correlation has an average absolute deviation of 1.7%, a bias of -0.04%, and an expanded uncertainty (at the 95% confidence level) of 4.75%.

Key words: density; reference correlation; squalane; transport properties; viscosity; pressure.

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1. Introduction

Most of the instruments for the measurement of viscosity require calibration and, for that purpose, certified reference liquids can be obtained commercially covering wide ranges of viscosity. Unfortunately, these viscosity standards are certified only for use at standard atmospheric pressure and their viscosities at high pressures are not generally available. There is therefore a need for fluids that can serve as viscosity reference standards at high pressures. In the oil industry, the viscosities of petroleum fluids are often measured under conditions of reservoir temperatures and pressures and, with ever deeper reservoirs being exploited, this necessitates calibration under similar conditions. The present work is aimed at establishing squalane as a viscosity reference material applicable at pressure - to 200 MPa and at temperature to 473 K.

The choice of a reference liquid involves several considerations. Ideally, it should be a single substance available commercially, with high chemical purity and at a reasonable cost. It should be chemically stable at the maximum working temperature, and should not be hygroscopic, toxic, nor excessively volatile. These requirements are difficult to satisfy even for a single area of application. However, for work on petroleum oils and similar applications, squalane appears to be a good choice as it satisfies all of the above criteria and has a viscosity of the order of 1 mPa·s at $T = 473$ K.

Recently, a correlation for the viscosity of squalane ($C_{30}H_{62}$, 2,6,10,15,19,23-hexamethyltetracosane, CAS No. 111-01-3) at standard atmospheric pressure was reported by our group.¹ This extends over the temperature range 273 to 373 K. Since then, new data have been published^{2, 3} and, in any event, there is a need to extend the correlation to high pressures and higher temperatures. Accordingly, in this work two new correlations are proposed that extend the temperature range to 473 K and that are applicable at pressures from 0.1 to 200 MPa. One is a function of density and temperature, based on the Assael-Dymond model, and the other a function of temperature and pressure, and is based on a modified Vogel-Fulcher-Tammann equation (VFT). As the first correlation is based on density, we have also critically examined high pressure density data in the literature and correlated the density over the same range of temperature and pressure as the viscosity, using the Tait equation.

TABLE 1. Density measurements for squalane at 0.1 MPa

1 st author	Year published	Technique employed ^a	Purity (%)	Uncertainty (%)	No. of points used	Temperature Range (K)
Primary Data						
Fernández ⁴	2013	OT	99.0	0.06	19	278-373
Fandiño ⁵	2010	VT	99.0	0.1	3	298-348
Trusler ³	2010	VW	99.0	0.2	2+6 ^b	338-473
Harris ⁶	2009	VT	99.0	0.006	12	273-363
Fandiño ⁷	2005	VT	99.0	0.01	9	278-353
Tripathi ⁸	2005	PC	> 99.0	0.07	1	298
Fermeglia ⁹	1999	VT	99.0	0.004	1	298
Kumagai ¹⁰	1995	PC	>99.0	0.04	3	293-333
Korosi ¹¹	1981	PC	na	0.04-0.08	4	293-473
Secondary Data						
Korotkovskii ¹²	2012	QD	99.5	0.01	28	298-413
Hata ¹³	2010	na	na	na	1	288
Dubey ¹⁴	2008	VT	99.0	0.25	3	298-308
Kumagai ¹⁵	2006	GP	na	0.4	3	293-333
Graaf ¹⁶	1992	WB	99.0	0.5	9	293-473
Kuss ¹⁷	1970	GP	na	4.0	4	298-353
Sax ¹⁸	1957	na	99.9	0.004	1	293

^aVW, Vibrating-Wire Densimeter; VT, Vibrating-Tube Densimeter; GP, Glass Piezometer; na, not given; PC, Pycnometer; OT, Oscillating-Tube Viscometer; QD, Quartz Densimeter; WB, Westphal balance.

^bThese data have been extrapolated from high pressure density values.

2. The Density Correlation

2.1. The Density Correlation for 0.1 MPa

Table 1 lists, to the best of our knowledge, all the investigators who have measured the density of squalane at 0.1 MPa. We note the following points about the various sets of data in the table. The measurements of Tomida *et al.*¹⁹ are excluded from the correlation as these are values interpolated from the 2006 measurements of Kumagai *et al.*¹⁵ These latter authors¹⁵ re-measured densities in 2006 as a function of pressure, but the values quoted are of inferior uncertainty to those determined in 1995 by this group.¹⁰ Therefore we have only used the 1995 measurements for the primary data set at 0.1 MPa with the exception of one density value at 273 K that is inconsistent with the rest of the data. We consider a datum to be inconsistent with the primary database when the residual is more than twice the standard deviation of the fit. The single measurement of Lal *et al.*²⁰ has been excluded, as this value was re-published by Tripathi.⁸ The data of Ciotta *et al.*²¹ were also excluded as the measurements were made at much higher pressures and could not be safely extrapolated to 0.1 MPa.

The measurements of Dubey and Sharma,¹⁴ Kuss and Taslimi,¹⁷ and Graaf *et al.*¹⁶ were excluded from the primary data set as they were of inferior uncertainties, 0.25, 4.0, 0.5% respectively. The

measurements of the first authors were re-published by Dubey *et al.*²² Hata and Tamoto¹³ quote no uncertainty for their single measurement, and this was placed in the secondary data set. The data of Korotkovskii *et al.*¹² show a distinctively different dependence on temperature to those of all other investigators, and thus these have also been considered as secondary data. The single measurement of Sax and Stross,¹⁸ was also excluded as insufficient information was given about the technique employed.

The remaining data³⁻¹¹ listed in Table 1, all obtained with very low uncertainties, form the primary data set. We note that the measurements of Trusler³ are extrapolated from high pressure isotherms to 0.1 MPa, though without any apparent increase of uncertainty.

Temperatures for all the data were converted to the ITS-90 temperature scale.²³ The primary data were fitted to an equation for the density, ρ_0 in kg/m³, as a function of the absolute temperature, T in K, as

$$\rho_0 = 996.28 - 0.6402 T . \quad (1)$$

This equation represents the selected primary data at 0.1 MPa from 273 K to 473 K. The percentage deviations of the experimental values from the values calculated by Eq.(1) are shown in Figure 1.

Table 2 summarizes comparisons of the primary data with the correlation. We have defined the percent deviation as $PCTDEV = 100(\rho_{o,exp} - \rho_{o,fit}) / \rho_{o,fit}$, where $\rho_{o,exp}$ is the experimental value of the density and $\rho_{o,fit}$ is the value calculated from the correlation. Thus, the average absolute percent deviation (AAD) is found with the expression $AAD = (\sum |PCTDEV|) / n$, where the summation is over all n points, and the bias, as a percentage, is found with the expression $bias = (\sum PCTDEV) / n$. The average absolute deviation of the fit is 0.03%, the bias -0.01%, and the expanded uncertainty at the 95% confidence level is 0.06%. The maximum deviation is 0.08% for a data point from Korosi and Kovats¹¹ at 293.15 K.

Figure 2 shows the percentage deviations of the secondary density data as a function of the temperature at 0.1 MPa, from the values calculated from Eq. (1). The same figure also includes the recommended values for the density of squalane from the American Petroleum Institute (API),²⁴ as well as the densities reported in the US National Institute of Science and Technology (NIST) Thermodynamic Research Center (TRC)²⁵ correlation tables. It is worthwhile noting that the recommended values from API²⁴ agree with the proposed correlation within 0.2%, and that the values reported in the NIST/TRC²⁵ tables agree within 0.5%.

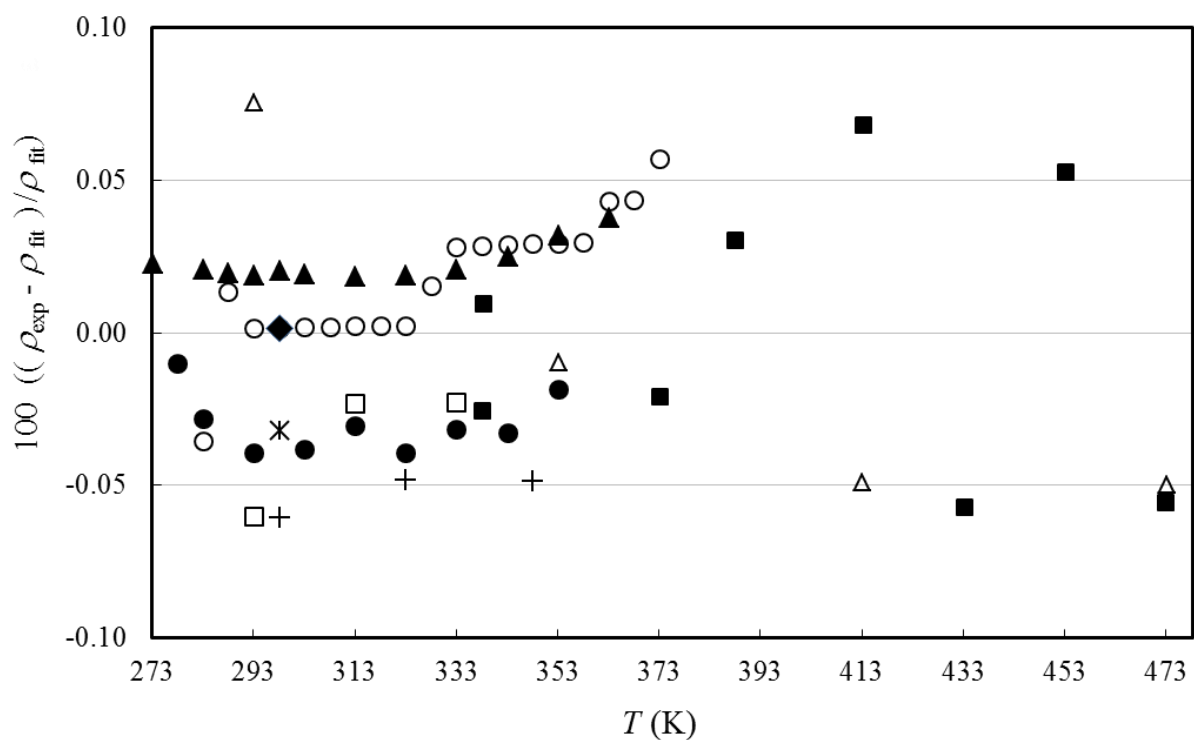


Figure 1. Percentage deviations for the primary density data as a function of temperature at 0.1 MPa, from the values calculated from Eq. (1): (O) Fernández *et al.*,⁴ (+), Fandiño *et al.*,⁵ (■) Trusler *et al.*,³ (▲) Harris,⁶ (●) Fandiño *et al.*,⁷ (◆) Tripathi,⁸ (*) Fermeglia and Torriano,⁹ (□) Kumagai and Takahashi,¹⁰ and (△) Korosi and Kovats.¹¹

TABLE 2. Evaluation of the squalane density correlation for the primary data at 0.1 MPa

1 st Author	Year Publ.	AAD (%)	Bias (%)
Fernández ⁴	2013	0.02	0.02
Fandiño ⁵	2010	0.05	-0.05
Trusler ³	2010	0.04	0.00
Harris ⁶	2009	0.02	0.02
Fandiño ⁷	2005	0.03	-0.03
Tripathi ⁸	2005	0.00	0.00
Fermeglia ⁹	1999	0.03	-0.03
Kumagai ¹⁰	1995	0.04	-0.04
Korosi ¹¹	1981	0.05	-0.01
Entire data set		0.03	-0.01

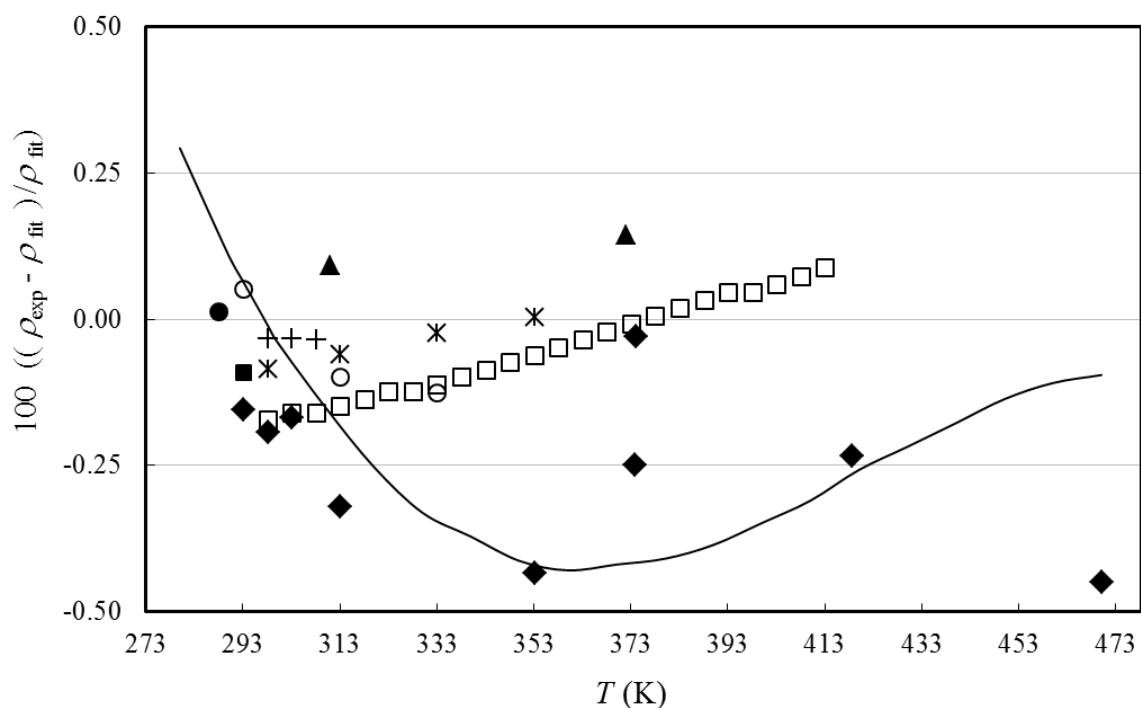


Figure 2. Percentage deviations for the secondary density data as a function of temperature at 0.1 MPa, from the values calculated from Eq. (1). (\square) Korotkovskii *et al.*,¹² (\bullet) Hata and Tamoto,¹³ (+) Dubey and Sharma,¹⁴ (\circ) Kumagai *et al.*,¹⁵ (\blacklozenge) Graaf *et al.*,¹⁶ ($*$) Kuss and Taslimi,¹⁷ (\blacksquare) Sax and Stross,¹⁸ (\blacktriangle) API,²⁴ and (—) NIST/TRC.²⁵

2.2. Density Correlation for High Pressure

Table 3 indicates all the investigators who have measured the density of squalane above atmospheric pressure. The investigations^{3, 5, 7, 15, 21} that contributed to the primary data for the 0.1 MPa correlation,¹ also make up the primary data set here. In addition, the data of Kuss and Taslimi,¹⁷ are included as primary values as they cover a very wide pressure range. The densities from Trusler *et al.*³ at pressures lower than 2 MPa were also not considered as they are inconsistent with the remaining points on the corresponding isotherms. In the case of the measurements by Ciotta *et al.*,²¹ the densities at 303.18 K and 15.58, 35.79, 45.77 and 55.77 MPa, as well as at 348.13 K and 115.8, 145.9 and 175.12 MPa, were excluded, as they are inconsistent with the rest of that data set.

TABLE 3. Density measurements for squalane at high pressures

1 st author	Year published	Technique employed ^a	Purity (%)	Uncertainty (%)	No. of data used	Temperature Range (K)	Pressure Range (MPa)
Fandiño ⁵	2010	VT	99.0	0.7-1.0	50	298-398	1-60
Trusler ³	2010	VW	99.0	0.2-0.6	70	338-473	21-202
Ciotta ²¹	2009	VW	99.0	0.2-0.6	25	303-448	1-176
Kumagai ¹⁵	2006	GP	na	0.4	12	273-333	10-30
Fandiño ⁷	2005	VT	99.0	0.01	90	278-353	1-45
Kuss ¹⁷	1970	GP	na	0.4	20	298-353	39-196

^aGP, Glass Piezometer; VT, Vibrating-Tube Densimeter; VW, Vibrating-Wire Densimeter; na, not given.

Temperatures for all data were converted to the ITS-90 temperature scale.²³ The primary data were fitted to a Tait equation for the density, ρ in kg/m³, as a function of the absolute temperature, T in K, and the pressure, p in MPa, as

$$\frac{\rho - \rho_o}{\rho} = 0.20 \log_{10} \left(\frac{B + p}{B + 0.1} \right), \quad (2)$$

where

$$B = 398.314 - 1.25406 T + 10.6525 \cdot 10^{-4} T^2 \quad (3)$$

In Eq. (2), the density at 0.1 MPa, ρ_o , is obtained from Eq. (1). We note that the coefficient of 0.20 in Eq.(2) is in full agreement with previous correlations of the densities of n -alkanes.²⁶ The equations above represent all the primary data from 273 K to 473 K and up to 200 MPa.

Table 4 summarizes comparisons of the primary data with the correlation. The average absolute deviation of the fit is 0.05%, the bias -0.004% and the expanded uncertainty at the 95% confidence level is 0.18%. Figures 3 to 5 show the percentage deviations of the primary density data as a function of the density, temperature, and pressure, from the values calculated from Eqs. (1) – (3).

TABLE 4. Evaluation of the squalane density correlation for the primary data at high pressures

1 st Author	Year Publ.	AAD (%)	Bias (%)
Fandiño ⁵	2010	0.03	0.01
Trusler ³	2010	0.07	-0.05
Ciotta ²¹	2009	0.15	0.09
Kumagai ¹⁵	2006	0.12	-0.11
Fandiño ⁷	2005	0.02	0.00
Kuss ¹⁷	1970	0.05	0.04
Entire data set		0.05	-0.004

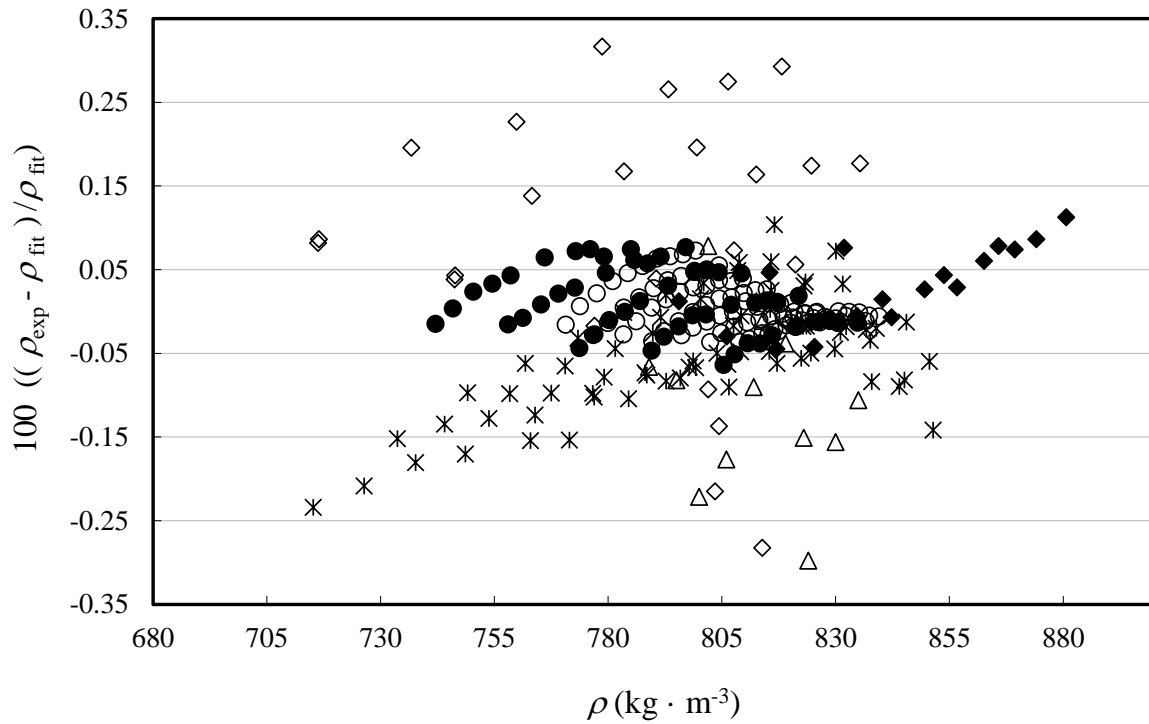


Figure 3. Percentage deviations for the primary density data at high pressures, as a function of density, from the values calculated from Eqs. (1) – (3): (●) Fandiño *et al.*⁵ (*) Trusler *et al.*,³ (◇) Ciotta *et al.*,²¹ (△) Kumagai *et al.*,¹⁵ (○) Fandiño *et al.*,⁷ (◆) Kuss and Taslimi.¹⁷

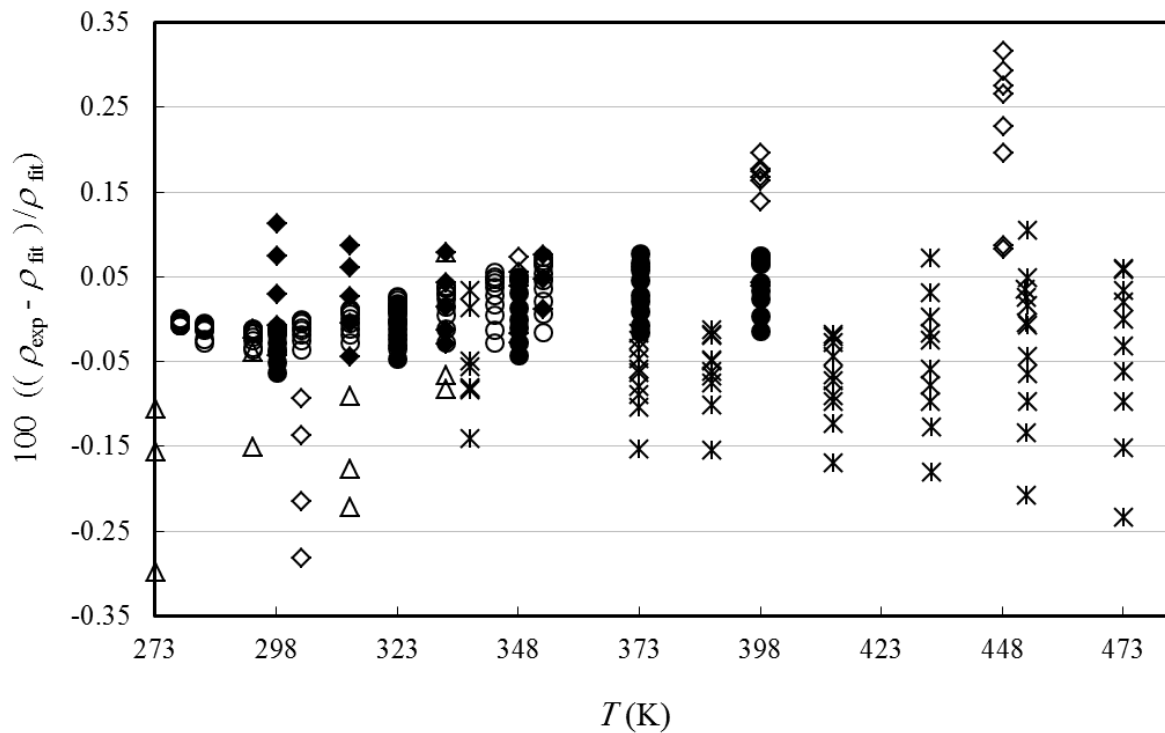


Figure 4. Percentage deviations for the primary density data at high pressures, as a function of temperature, from the values calculated from Eqs. (1) – (3): (●) Fandiño *et al.*,⁵ (*) Trusler *et al.*,³ (◇) Ciotta *et al.*,²¹ (△) Kumagai *et al.*,¹⁵ (○) Fandiño *et al.*,⁷ (◆) Kuss and Taslimi.¹⁷

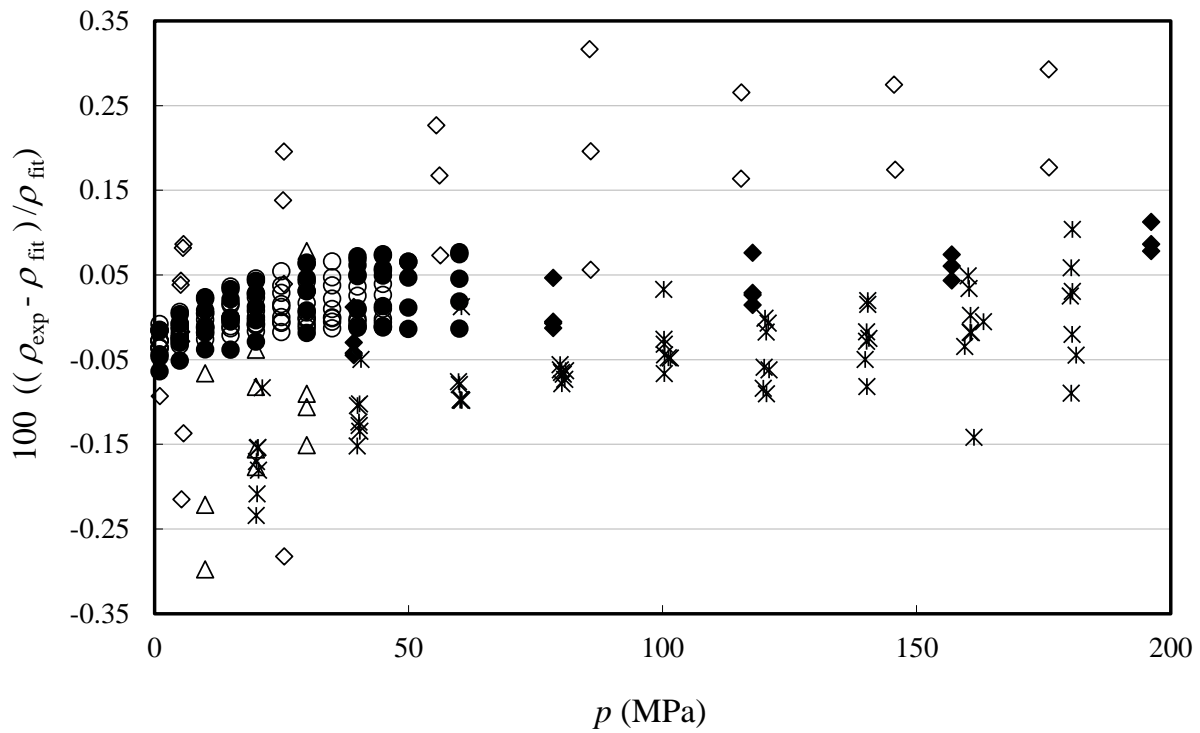


Figure 5. Percentage deviations for the primary density data at high pressures, as a function of pressure, from the values calculated from Eqs. (1) – (3): (●) Fandiño *et al.*,⁵ (*) Trusler *et al.*,³ (◇) Ciotta *et al.*,²¹ (△) Kumagai *et al.*,¹⁵ (○) Fandiño *et al.*,⁷ (◆) Kuss and Taslimi.¹⁷

3. The High Pressure Viscosity Correlation

In a recent publication,¹ we have proposed a reference correlation for the viscosity of squalane at 0.1 MPa. This covers the temperature range from 273 to 373 K, with an average absolute deviation of 0.67%, and an expanded uncertainty (at the 95% confidence level) of 1.5%. Since that time, new measurements^{2, 3} have been published, allowing the extension of the reference correlation, for both temperature and pressure.

TABLE 5. Viscosity measurements for squalane at high pressures

1 st author	Year published	Technique employed ^a	Purity ^b (%)	Uncertainty (%)	No of data	Temperature Range (K)	Pressure Range (MPa)
Primary Data							
Comuñas ² (UNSW ^d)	2013	FB	99.0	2.0	24	313-363	0.1-200 ^c
Comuñas ² (UPPA ^d)	2013	FB	99.0	3.0	28	303-348	20-200
Comuñas ² (UPPA ^d)	2013	QCR	99.0	2.0	85	293-333	0.1-81
Mylona ²⁷	2013	VW	99.0	1.0	31	298-338	0.1-20
Trusler ³	2010	VW	99.0	2.0	89	338-473	0.1-202
Ciotta ²¹	2009	VW	99.0	2.0	32	303-448	1-176
Harris ⁶	2009	FB	99.0	2.0	118	278-353	0.1-200 ^c
Tomida ¹⁹	2007	RB	98.0	3.0	12	293-353	10-20
Kumagai ¹⁵	2006	FB	98.0	2.9	12	293-333	0.1-30
Pensado ²⁸	2006	RB	99.0	3.0	84	303-353	0.1-60
Secondary Data							
Comuñas ² (USC ^d)	2013	FB-LPT	99.0	5.0	34	313-363	10-200 ^c
Hata ¹³	2010	RB	na	na	18	313-423	0.1-200 ^c
Bair ²⁹	2006	FB	99.0	na	16	293-373	0.1-200 ^c
Bair ³⁰	2002	FB	na	na	11	303-373	0.1-146 ^c
Krahn ³¹	1994	RB	99.0	2.0	18	298-453	0.1-195
Kuss ³²	1972	FB	na	1.3	27	298-313	0.1-98

^aRB, rolling ball; C, capillary; VW vibrating wire; FB falling body; QCR quartz crystal resonator.

^bna, not available

^cRestricted to 200 MPa pressure (upper pressure limit for density).

^dMeasurements of different investigators, all reported in the same paper: UNSW, University of New South Wales; UPPA, University of Pau; USC, University of Santiago de Compostela.

In Table 5, all the available measurements for the viscosity of squalane at high pressures are shown. Since the density correlation is valid between 278 and 473 K at pressures to 200 MPa, these limits also apply to the two viscosity correlations used in this work. The falling-body measurements of USC (from Comuñas *et al.*²) which have an uncertainty of 5%, are considered as secondary data. In addition, the very high-pressure measurements of Bair^{29, 30} are put in the secondary data set, as they show significant discrepancies from the results of all other investigators in the moderate pressure region considered in this work. The measurements of Hata and Tamoto¹³ are also considered as secondary data, as no uncertainty nor purity were given. Finally, the older measurements of Krahn and Luft,³¹ and of Kuss and Golly,³² are put in the secondary data set as they show large deviations from the other sets. The remaining sets of data, all with uncertainties of less than 3%, form the primary data set. Given the temperature and pressure limits imposed by the density correlation, it can be seen that only two sets^{2, 6} in Table 5 extend above the pressure limit of the present equation of state (200 MPa).

Figure 6 shows the temperature and pressure coordinates of data points retained for the primary viscosity correlations. The T - p area of the primary viscosity data used is not rectangular. The reader

should be aware that extrapolation outside this area should be avoided for both correlations discussed below.

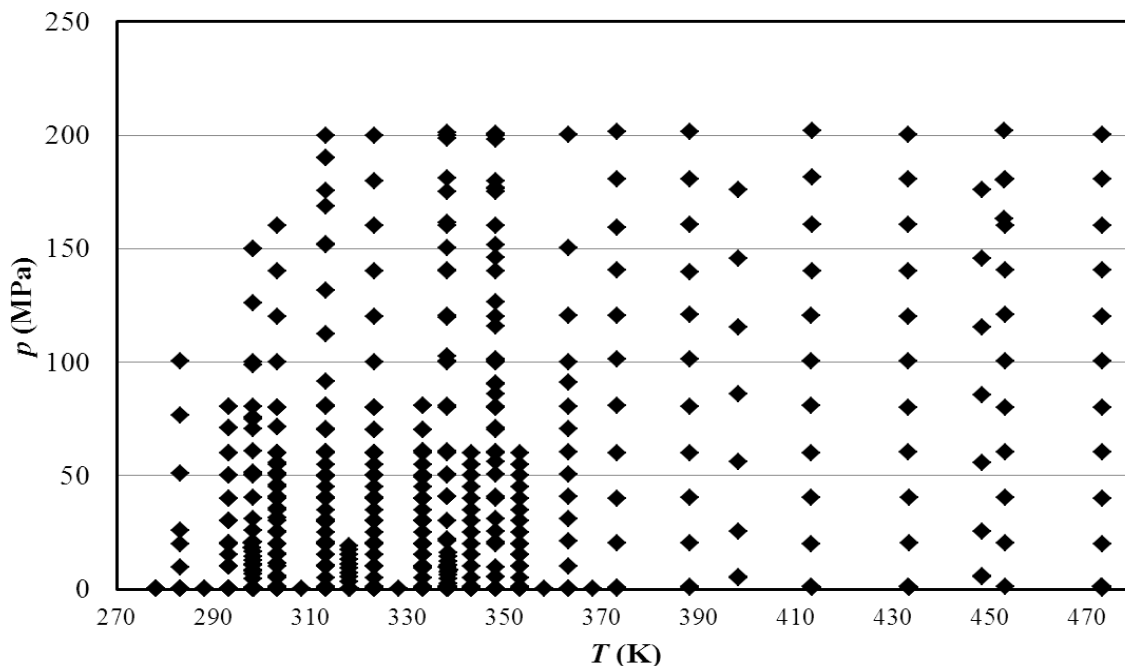


Figure 6. Temperature and pressure coordinates of data points retained for the primary viscosity correlations.

Finally it should be noted that a reference correlation for the viscosity of squalane at 0.1 MPa based on the VFT equation has already been published.¹ To ensure consistency between that correlation and the present one, the data employed in that paper also form part of the primary data set.

In the following sections, two correlations for the viscosity of squalane are presented, one as a function of density and temperature and the other as a function of temperature and pressure.

3.1 Viscosity Correlation as a Function of Density and Temperature

In order to correlate the viscosity at high densities, the theoretically based scheme of Assael and Dymond³³ has been employed. This scheme has been adopted as it is based on hard-sphere theory considerations, and it correlates the viscosity as a function of the density and temperature, rather than the pressure and temperature. Assael and Dymond³³ showed that one can employ a reduced, dimensionless viscosity, η^* , defined in terms of the viscosity of a dilute gas of hard spheres (η_0) of diameter σ , and calculable from experimental quantities, as

$$\begin{aligned}
\eta^* &= (\eta / \eta_0)(V_m / V_0)^{2/3} \\
&= \frac{16}{5}(2N_A)^{1/3} \left(\frac{\pi}{MRT} \right)^{1/2} V_m^{2/3} \eta \quad . \\
&= F_\eta (V_r)
\end{aligned} \tag{4}$$

In the above equation, η is the experimental viscosity of the fluid, N_A is Avogadro's constant (mol^{-1}), M (kg/mol) is the molar mass, R ($\text{J mol}^{-1} \text{K}^{-1}$) is the universal gas constant, T (K) the absolute temperature, and V_m (m^3/mol) the molar volume. In the original scheme, $F_\eta(V_r)$ denoted a universal reference function for the reduced volume $V_r = (V_m/V_0)$, obtained by employing a large amount of experimental data for dense monatomic gases, with $V_0 = N_A \sigma^3 / \sqrt{2}$ ($\text{m}^3 \text{mol}^{-1}$) as a characteristic molar volume dependent only on the temperature. In the original theory, V_0 is the equivalent volume of close-packed hard spheres, with a temperature dependent diameter to allow modeling of real fluids with soft, repulsive intermolecular potentials. If F_η is known, experimental measurements of a particular liquid can be correlated over a wide range of temperatures and pressures, by obtaining $V_0 = f(T)$. This scheme has been successfully applied to n -alkanes,³³ aromatic hydrocarbons³⁴ and many other fluids.^{35, 36} More recently, an attempt has been made to extrapolate this scheme to high-viscosity fluids.³⁷

However, as the original scheme was developed for low-viscosity fluids, and the recent attempt³⁶ to extrapolate this to high-viscosity fluids was based on only a few fluids, it could not be applied here. Instead a slightly different approach was preferred with the function F_η being obtained directly from the primary experimental measurements (see Table 5), by expressing η^* as a function of $\log_{10} V_m$. A horizontal translation of isotherms produces a characteristic quantity V_f (m^3/mol) at a given temperature allowing scaling onto a single curve. For squalane, this process yields

$$\log_{10} \eta^* = -23274.3831 - 21623.6741\Psi - 6698.8037\Psi^2 - 692.0224\Psi^3 \quad . \tag{5}$$

where $\Psi = \log_{10}(V_m/V_f)$, and

$$\log_{10} V_f = (0.308862 + 1.538769 \times 10^{-3}T + 2.712304 \times 10^{-6}T^2 - 1.774377 \times 10^{-9}T^3) \tag{6}$$

Eqs.(4)-(6) form a consistent scheme through which the viscosity can be calculated as a function of the density and the temperature employing Eqs.(1)-(3).

The primary data given in Table 5 cover a very broad viscosity range from 0.85 to 954 mPa s. This range is too wide to be covered with low uncertainty with a single correlation, and it was found preferable to examine it in two regions.

Figures 7, 8, and 9 show all primary data in the temperature range 320 to 473 K at pressures up to 200 MPa (the pressure limit imposed by the density correlation) as a function of the density, temperature and pressure; Table 6 summarizes the comparisons of the primary data with the scheme of

Eqs.(1) – (6). The average absolute deviation of the fit is 1.41%, the bias -0.09%, and the expanded uncertainty at the 95% confidence level is just under 3%. Finally, by examining Figure 7, it can be seen that our previous reference correlation¹ for the viscosity of squalane with an expanded uncertainty of 1.5%, at 0.1 MPa and in the temperature range 273 to 373 K, agrees very well with the present correlation.

Figure 10 shows the primary data in the entire temperature range given by the density correlation, that is, from 278 to 473 K. It can be seen that below 320 K the deviations increase to a maximum of 20%. The model does not well accommodate the rapid increase in viscosity at low temperatures, but does perform very well at high temperatures (above around 410 K). Figure 11, shows the percentage deviations of the secondary viscosity data in the temperature range 278 to 473 K at pressures to 200 MPa, as a function of the temperature from the values calculated from Eqs. (1) – (6).

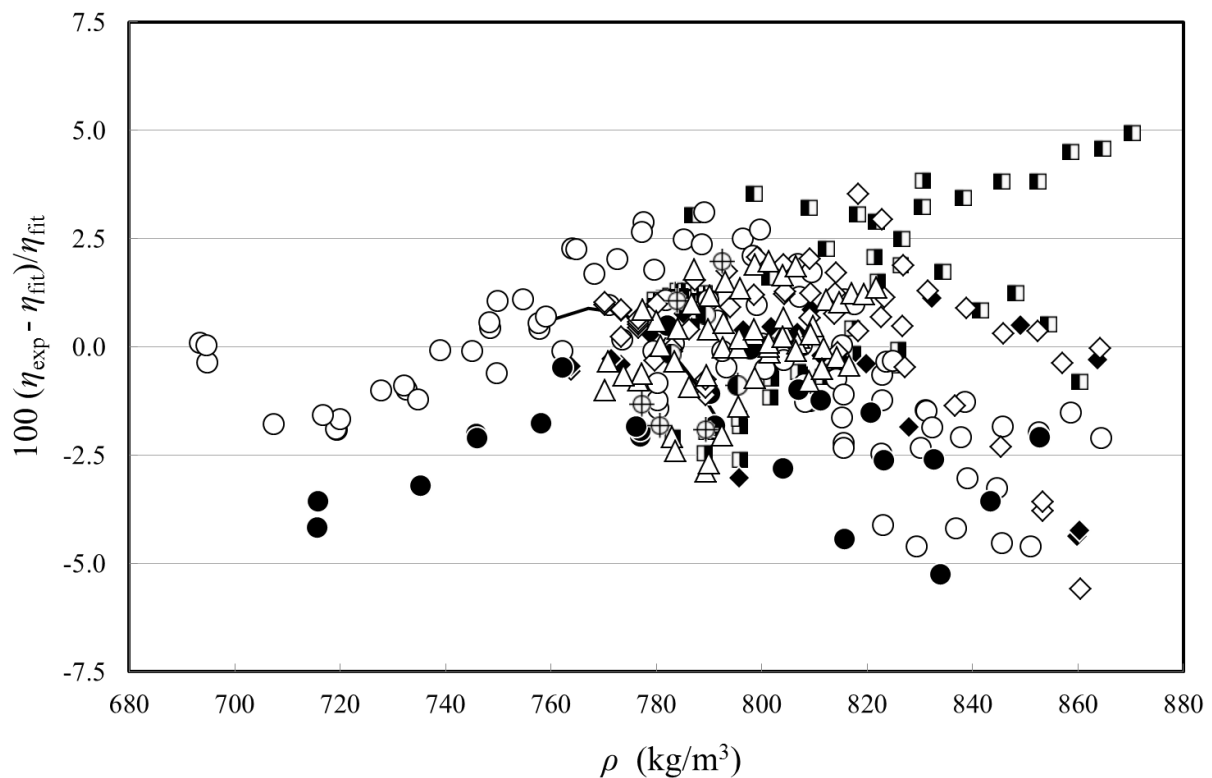


Figure 7. Percentage deviations for the primary viscosity data in the temperature range 320 to 473 K and up to 200 MPa, as a function of density, from the values calculated from Eqs. (1) – (6). (◆) Comuñas *et al.*² (UNSW); (■) Comuñas *et al.*² (UPPA-FB); (▣) Comuñas *et al.*² (UPPA-QCR); (+) Mylona *et al.*²⁷; (○) Trusler *et al.*³; (●) Ciotta *et al.*²¹; (◇) Harris⁶; (⊕) Tomida *et al.*¹⁹; (◐) Kumagai *et al.*¹⁵; (△) Pensado *et al.*²⁸; (—) Comuñas *et al.*¹

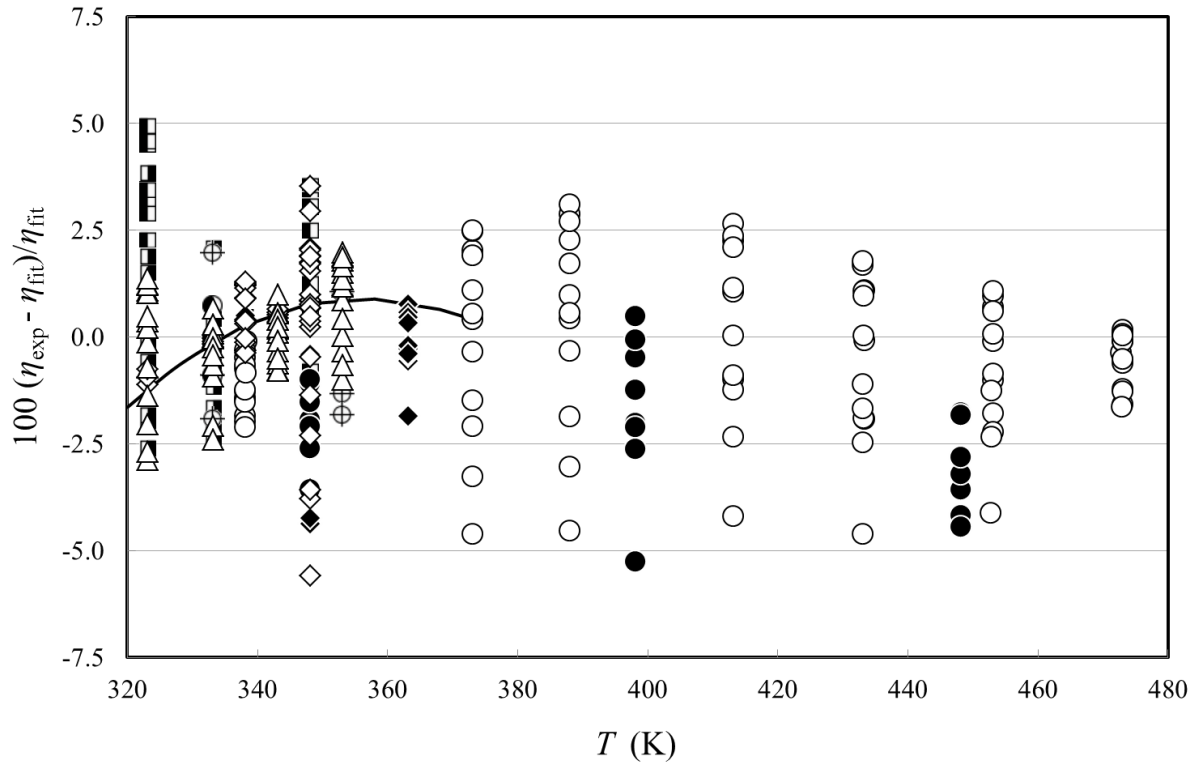


Figure 8. Percentage deviations for the primary viscosity data in the temperature range 320 to 473 K and up to 200 MPa, as a function of temperature, from the values calculated from Eqs. (1) – (6). (◆) Comuñas *et al.*² (UNSW); (■) Comuñas *et al.*² (UPPA-FB); (▣) Comuñas *et al.*² (UPPA-QCR); (+) Mylona *et al.*²⁷; (○) Trusler *et al.*³; (●) Ciotta *et al.*²¹; (◇) Harris⁶; (⊕) Tomida *et al.*¹⁹; (●) Kumagai *et al.*¹⁵; (△) Pensado *et al.*²⁸; (—) Comuñas *et al.*¹

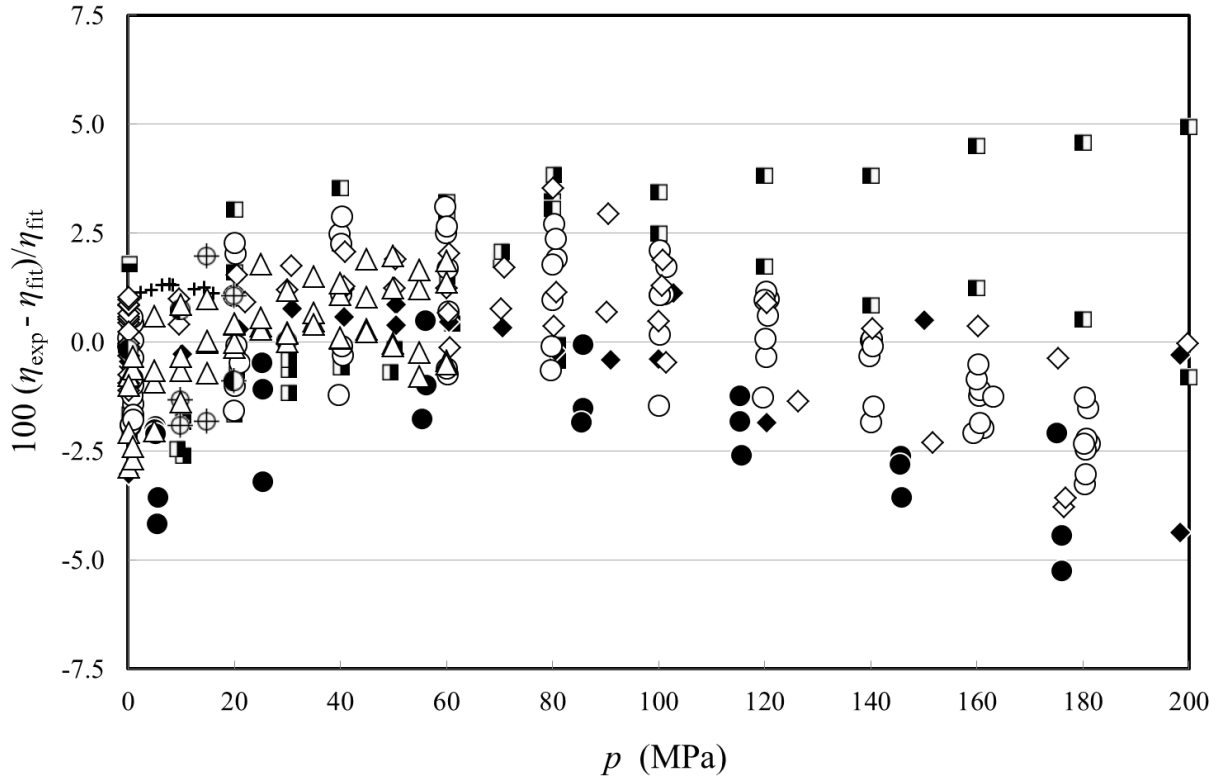


Figure 9. Percentage deviations for the primary viscosity data in the temperature range 320 to 473 K and up to 200 MPa, as a function of pressure, from the values calculated from Eqs. (1) – (6). (◆) Comuñas *et al.*² (UNSW); (■) Comuñas *et al.*² (UPPA-FB); (▣) Comuñas *et al.*² (UPPA-QCR); (+) Mylona *et al.*²⁷; (○) Trusler *et al.*³; (●) Ciotta *et al.*²¹; (◇) Harris⁶; (⊕) Tomida *et al.*¹⁹; (◐) Kumagai *et al.*¹⁵; (△) Pensado *et al.*²⁸

TABLE 6. Evaluation of the squalane viscosity correlation as a function of density and temperature for the primary data in the temperature range 320 to 473 K at pressures up to 200 MPa

1 st Author	Year Publ.	AAD (%)	Bias (%)
Comuñas ² (UNSW)	2013	1.34	-0.91
Comuñas ² (UPPA)	2013	2.79	2.71
Comuñas ² (UPPA)	2013	1.32	-0.17
Mylona ²⁷	2013	1.16	1.16
Trusler ³	2010	1.45	-0.40
Ciotta ²¹	2009	2.25	-2.11
Harris ⁶	2009	1.21	0.39
Tomida ¹⁹	2007	1.51	-0.51
Kumagai ¹⁵	2006	0.46	-0.09
Pensado ²⁸	2006	0.86	0.08
Entire data set		1.41	-0.09

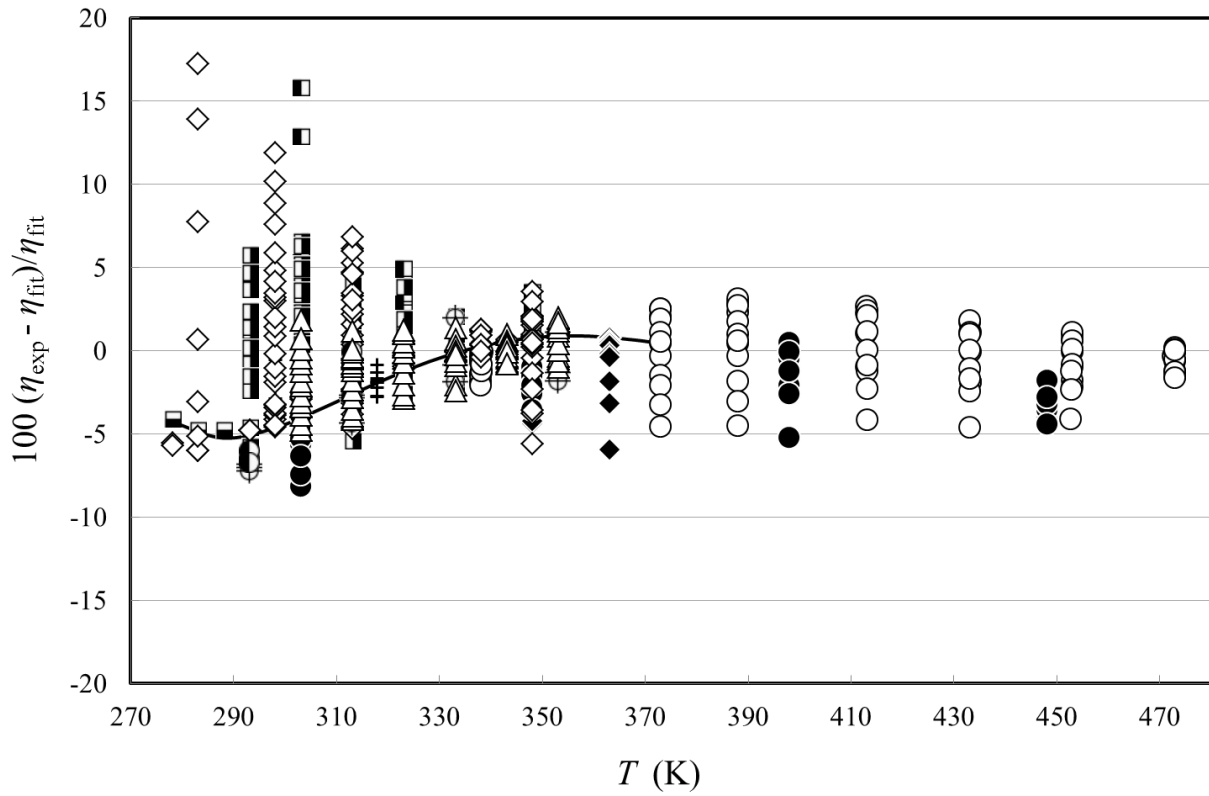


Figure 10. Percentage deviations for the primary viscosity data in the temperature range 278 to 473 K at pressures to 200 MPa as a function of temperature from the values calculated from Eqs. (1) – (6). (◆) Comuñas *et al.*² (UNSW); (■) Comuñas *et al.*² (UPPA-FB); (□) Comuñas *et al.*² (UPPA-QCR); (+) Mylona *et al.*²⁷; (○) Trusler *et al.*³; (●) Ciotta *et al.*²¹; (◇) Harris⁶; (⊕) Tomida *et al.*¹⁹; (●) Kumagai *et al.*¹⁵; (△) Pensado *et al.*²⁸ (—) Comuñas *et al.*¹

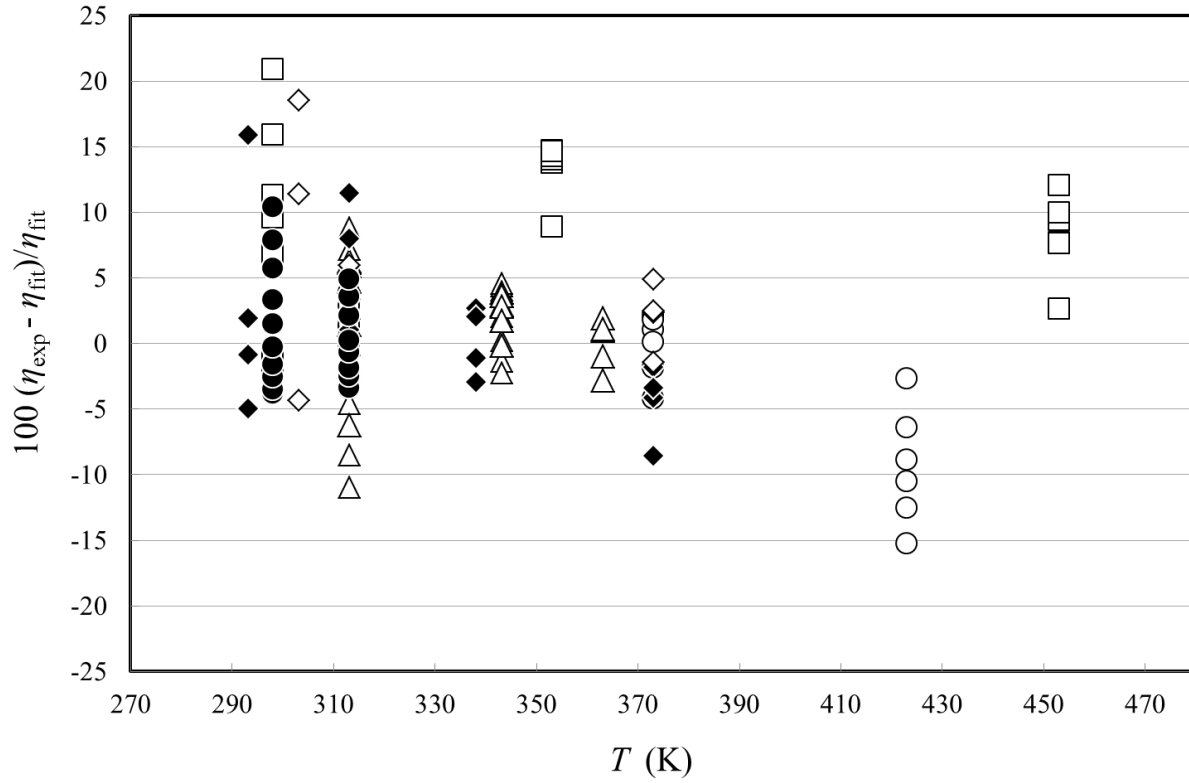


Figure 11. Percentage deviations for the secondary viscosity data in the temperature range 278 to 473 K at pressures to 200 MPa, as a function of temperature from the values calculated from Eqs. (1) – (6). (Δ) Comuñas *et al.*² (USC); (\circ) Hata and Tamoto¹³; (\blacklozenge) Bair²⁹; (\diamond) Bair³⁰; (\square) Krahn and Luft³¹; (\bullet) Kuss and Golly.³²

3.2 Viscosity Correlation as a Function of Pressure and Temperature

The viscosity data for squalane were also correlated as a function of pressure and temperature, by employing a modified VFT equation, which is known to be suitable at high viscosities.^{2,6} This also has eight parameters and employs a third degree polynomial in the pressure as follows:

$$\eta = A \exp \left(a_1 \Delta p + a_2 \Delta p^2 + \frac{B + b_1 \Delta p + b_2 \Delta p^2 + b_3 \Delta p^3}{T - C} \right) \quad (7)$$

where $\Delta p = p - p_{\text{ref}}$. Comuñas *et al.*² have used this correlation equation (7) very recently and Ducoulombier *et al.*³⁸ and Paredes *et al.*^{39,40} have used very similar equations in the past. In equation (7) we use 0.1 MPa as reference pressure. Thus, when p is also equal to 0.1 MPa this equation collapses to:

$$\eta = A \exp \left(\frac{B}{T - C} \right) \quad (8)$$

The VFT form, equation (8), has been used by Comuñas et al.¹ in proposing a reference correlation for the viscosity of squalane at 0.1 MPa, but is valid only over the temperature interval 273 to 373 K. As in this work the maximum temperature is extended to 473 K. Instead of using the previously obtained A , B and C regression parameters,¹ we have performed a new fit for Eq. (7), considering all the primary viscosity data in the 278-473 K interval and up to 200 MPa.

In Table 7, the parameter values are given to six significant figures in order to not introduce changes in calculated viscosities linked to rounding of the parameters in the calculations. The AAD obtained is 1.69%, the bias is -0.04% and the maximum absolute deviation is 9.1%. The expanded uncertainty at the 95% confidence level is just under 4.75%. Note that for viscosity values at 0.1 MPa with the new A , B and C values we obtain an AAD of 1.2% and bias 0.48%, close to the previous results.¹

TABLE 7. Parameters and relative deviations for VFT model, equation (7)

Parameters	Values
A (mPa·s)	0.0831311
B (K)	727.325
C (K)	172.993
$a_1 \cdot 10^3$ (MPa ⁻¹)	2.06832
$a_2 \cdot 10^6$ (MPa ⁻²)	1.31522
b_1 (MPa ⁻¹ · K)	2.60294
$b_2 \cdot 10^3$ (MPa ⁻² · K)	-4.19779
$b_3 \cdot 10^6$ (MPa ⁻³ · K)	6.10051
AAD (%)	1.69
Bias (%)	-0.04

In the previous subsection, 3.1, the density correlation is limited to 200 MPa as there are reliable direct experimental data for the density only below that pressure. Above 200 MPa, when needed, the density can be generally indirectly evaluated (see, for instance, the extrapolation method used by Harris⁶). In practice, the working equations of most experimental viscosity methods require the density as an input but fortunately the viscosity value is not very sensitive to the accuracy of the density in most of these methods. For instance, for the falling body method,² an uncertainty of 1% in the density (which is a big uncertainty) implies a relative uncertainty of less than 0.2% in the viscosity due the large difference between the density of the sinker and that of squalane. Nevertheless, the uncertainty in the viscosity is probably larger at high pressures than at low pressures. Consequently, we have limited the viscosity correlation to pressures below 200 MPa as the viscosity values are then linked to reliable direct density measurements. Note that, in theory, the proposed viscosity (T, p) correlation, Eq.(7), could have been applied to pressures higher than 200 MPa because it is independent of the density. For pressures higher than 200 MPa the reader can use the correlation proposed by Comuñas *et al.*² to 350

MPa, though this may be a less accurate correlation, being obtained with a smaller data set over a smaller temperature interval (below 363.15 K).

Figures 12, 13 and 14 show all the primary data in the temperature range 278 to 473 K at pressures up to 200 MPa as a function of the density, temperature and pressure. Table 8 summarizes the comparison of the primary data with the scheme of Eq. (7). Finally, by examining Figure 13, it can be seen that our previous reference correlation¹ for the viscosity of squalane (which has an expanded uncertainty of 1.5%, at 0.1 MPa and in the temperature range 273 to 373 K), agrees very well with the present correlation. Figure 15 shows the percentage deviations for the secondary viscosity data in the temperature range 278 to 473 K at pressures to 200 MPa, as a function of the temperature for the values calculated from Eq. (7). A comparison of Figures (10) and (13) shows that this model gives a better fit to the data at low temperatures than the Assael-Dymond model, Eq. (4) to (6), at the cost of a poorer fit at higher temperatures.

TABLE 8. Evaluation of the squalane viscosity correlation as a function of pressure and temperature for the primary data in the temperature range 278 to 473 K and up to 200 MPa

1 st Author	Year Publ.	AAD (%)	Bias (%)
Comuñas ² (UNSW ^d)	2013	2.28	-2.17
Comuñas ² (UPPA ^d)	2013	1.88	1.59
Comuñas ² (UPPA ^d)	2013	1.45	0.33
Mylona ²⁷	2013	1.23	1.23
Trusler ³	2010	2.98	0.39
Ciotta ²¹	2009	2.98	-2.37
Harris ⁶	2009	1.13	0.16
Tomida ¹⁹	2007	2.02	-1.66
Kumagai ¹⁵	2006	1.93	-0.29
Pensado ²⁸	2006	0.75	-0.41
Entire data set		1.69	-0.04

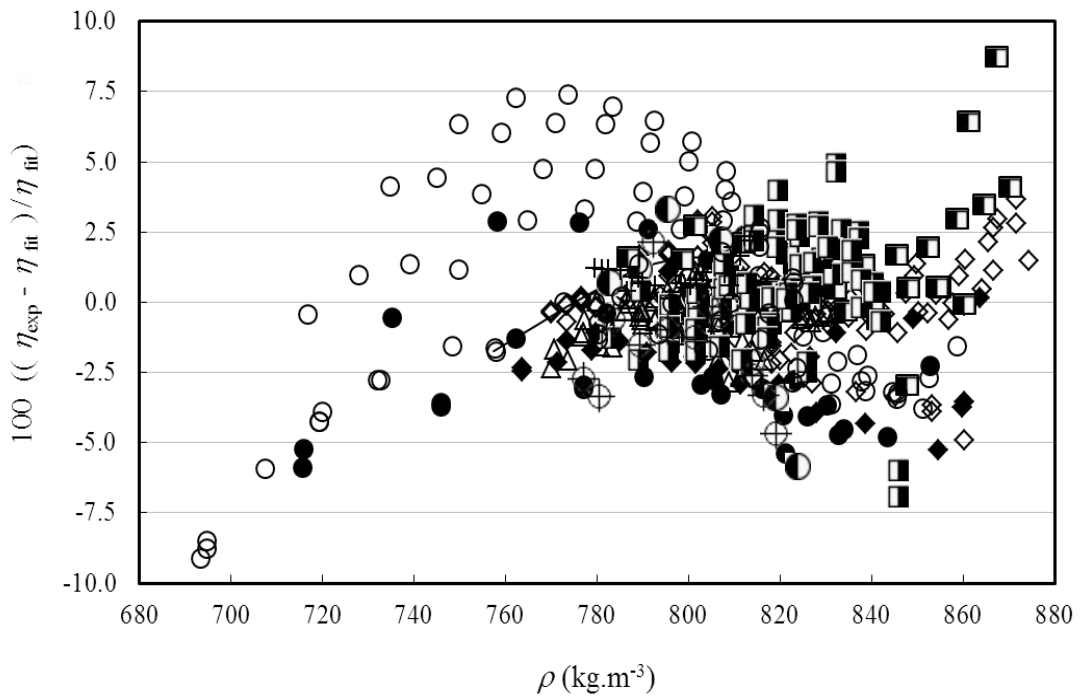


Figure 12. Percentage deviations for the primary viscosity data in the temperature range 278 to 473 K and up to 200 MPa, as a function of density, from the values calculated from Eq. (7). (\blacklozenge) Comuñas *et al.*² (UNSW); (\blacksquare) Comuñas *et al.*² (UPPA-FB); (\blacksquare) Comuñas *et al.*² (UPPA-QCR); (+) Mylona *et al.*²⁷; (\circ) Trusler *et al.*³; (\circ) Ciotta *et al.*²¹; (\diamond) Harris⁶; (\oplus) Tomida *et al.*¹⁹; (\bullet) Kumagai *et al.*¹⁵; (\triangle) Pensado *et al.*²⁸; (—) Comuñas *et al.*¹

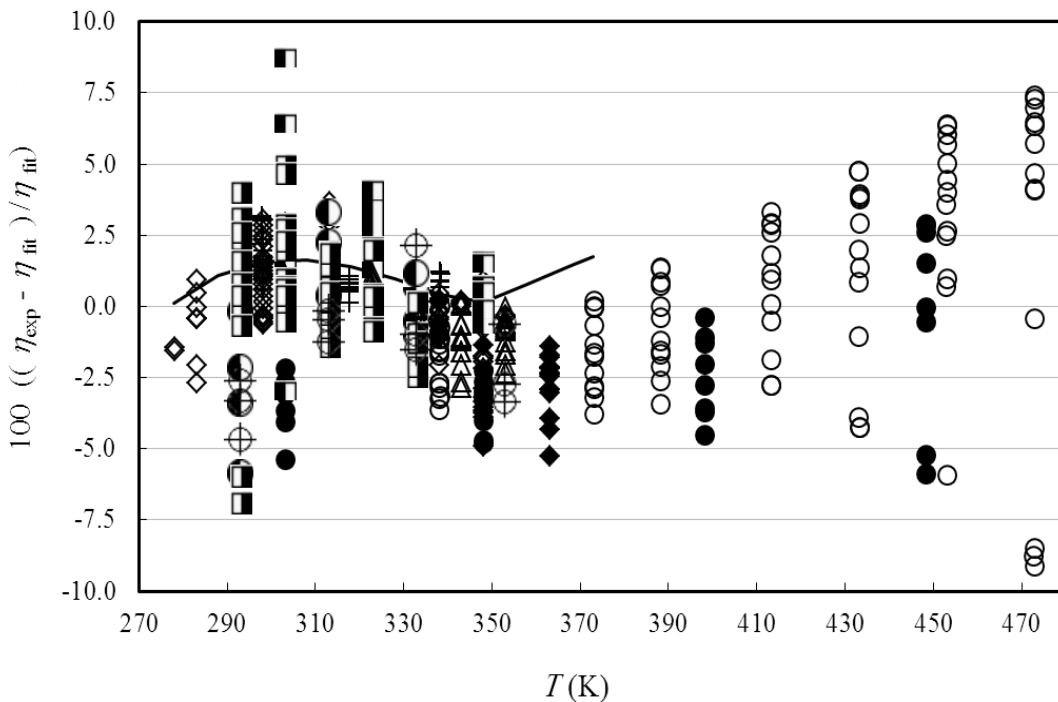


Figure 13. Percentage deviations for the primary viscosity data in the temperature range 278 to 473 K and up to 200 MPa, as a function of temperature, from the values calculated from Eq. (7). (\blacklozenge) Comuñas *et al.*² (UNSW); (\blacksquare) Comuñas *et al.*² (UPPA-FB); (\blacksquare) Comuñas *et al.*² (UPPA-QCR); (+) Mylona *et al.*²⁷; (\circ) Trusler *et al.*³; (\bullet) Ciotta *et al.*²¹; (\diamond) Harris⁶; (\oplus) Tomida *et al.*¹⁹; (\bullet) Kumagai *et al.*¹⁵; (\triangle) Pensado *et al.*²⁸; (—) Comuñas *et al.*¹

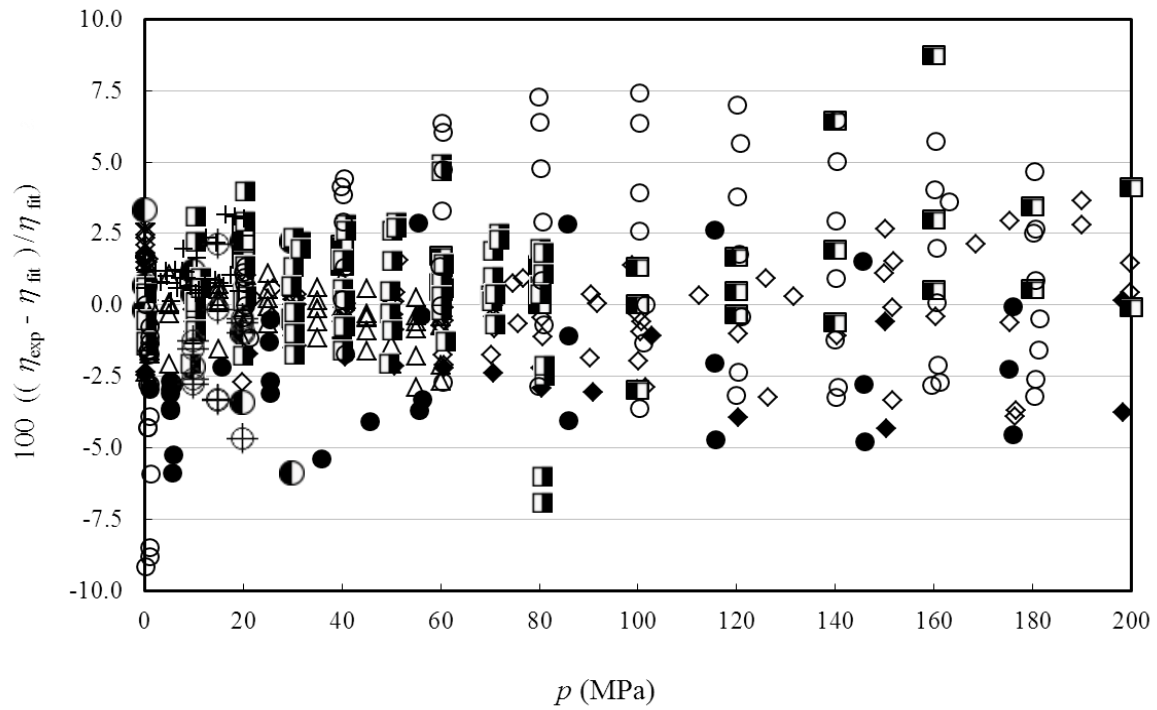


Figure 14. Percentage deviations for the primary viscosity data in the temperature range 278 to 473 K and up to 200 MPa, as a function of pressure, from the values calculated from Eq. (7). (\blacklozenge) Comuñas *et al.*² (UNSW); (\blacksquare) Comuñas *et al.*² (UPPA-FB); (\square) Comuñas *et al.*² (UPPA-QCR); (+) Mylona *et al.*²⁷; (\circ) Trusler *et al.*³; (\bullet) Ciotta *et al.*²¹; (\diamond) Harris⁶; (\oplus) Tomida *et al.*¹⁹; (\odot) Kumagai *et al.*¹⁵; (\triangle) Pensado *et al.*²⁸

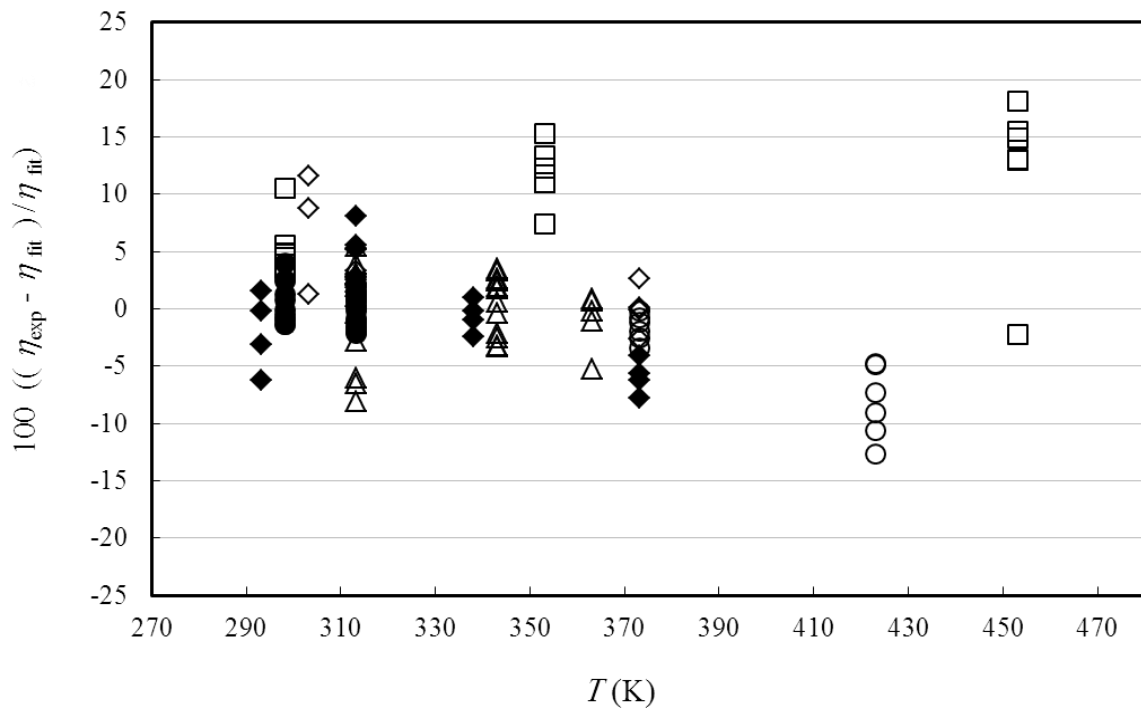


Figure 15. Percentage deviations for the secondary viscosity data in the temperature range 278 to 473 K at pressures to 200 MPa, as a function of temperature from the values calculated from Eq. (7). (\triangle) Comuñas *et al.*² (USC); (\circ) Hata and Tamoto¹³; (\blacklozenge) Bair²⁹; (\diamond) Bair³⁰; (\square) Krahn and Luft³¹; (\bullet) Kuss and Golly.³²

4. Conclusion

New reference correlations for the density and viscosity of squalane are presented. These correlations are based on critically evaluated experimental data taken from the literature.

In the case of the density, the correlation, employing the Tait equation, is valid from 273 to 473 K at pressures to 200 MPa. At 0.1 MPa, it shows an average absolute deviation of 0.03%, a bias of -0.01%, and an expanded uncertainty (at the 95% confidence level) of 0.06%. Over the whole range of pressure, the density correlation shows an average absolute deviation of 0.05%, a bias of -0.004%, and an expanded uncertainty (at the 95% confidence level) of 0.18%.

The first viscosity correlation expresses the viscosity as a function of density and temperature, and is based on the Assael-Dymond model, Eq. (4) to (6). It is slightly superior at higher temperatures, the region of primary interest in applications, but gives a poorer fit at low temperatures when the viscosity is strongly temperature dependent. This correlation covers the temperature range from 320 to 473 K at pressures to 200 MPa, and has an average absolute deviation of 1.41%, a bias of -0.09%, and an expanded uncertainty (at the 95% confidence level) of 3%. Below 320 K, the deviations from the present scheme rise to a maximum of 20%.

The second correlation is based on a modified Vogel-Fulcher-Tammann equation, with the viscosity expressed as a function of pressure and temperature, Eq. (7). It is superior to the first at low temperatures, but inferior at higher temperatures. This correlation covers a broader temperature range from 278 to 473 K at pressures to 200 MPa, and has an average absolute deviation of 1.69%, a bias of -0.04%, and an expanded uncertainty (at the 95% confidence level) of 4.75%.

Finally, Table 9 gives some selected reference values for density and viscosity calculated from Eq.(1) to (3) (density), and Eq.(5) to (6) or Eq. (7) (viscosity).

TABLE 9: Some selected reference values

T (K)	p (MPa)	ρ_{corr} (kg.m ⁻³)	η (mPa.s)	
			Eq (1)-(3)	Corr Eq. (4)-(6) Corr Eq. (7)
333.15	0.1	783.0	7.86	7.80
353.15	0.1	770.2	4.65	4.71
373.15	0.1	757.4	3.08	3.15
393.15	0.1	744.6	2.21	2.26
413.15	0.1	731.8	1.68	1.72
433.15	0.1	719.0	1.33	1.36
453.15	0.1	706.2	1.06	1.11
473.15	0.1	693.4	0.85	0.94
333.15	100	833.6	37.57	38.38
353.15	100	824.3	19.35	19.84
373.15	100	815.4	11.43	11.71
393.15	100	806.7	7.50	7.60
413.15	100	798.2	5.33	5.30
433.15	100	790.0	4.02	3.91
453.15	100	781.8	3.17	3.01
473.15	100	773.5	2.58	2.40
333.15	200	866.2	137.42	137.09
353.15	200	858.3	63.16	62.70
373.15	200	850.7	33.80	33.53
393.15	200	843.4	20.35	20.09
413.15	200	836.3	13.42	13.11
433.15	200	829.4	9.47	9.13
453.15	200	822.4	7.04	6.70
473.15	200	815.3	5.42	5.12

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