Reference Correlation of the Viscosity of Squalane from 273 to 373 K at 0.1 MPa

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The paper presents a new reference correlation for the viscosity of squalane at 0.1 MPa. The correlation should be valuable as it is the first to cover a moderately high viscosity range, from 3 to 118 mPa s. It is based on new viscosity measurements carried out for this work, as well as other critically evaluated experimental viscosity data from the literature. The correlation is valid from 273 K to 373 K at 0.1 MPa. The average absolute percentage deviation of the fit is 0.67, and the expanded uncertainty, with a coverage factor *k* = 2, is 1.5%.

Key words: Reference correlation; squalane; transport properties; viscosity.

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1. Introduction

Water has long been established as the primary viscosity reference fluid, despite the limitations imposed by its phase diagram and the relative insensitivity of its viscosity to applied pressure.[1] Over the last three decades the International Association for Transport Properties, IATP (formerly known as Subcommittee of Transport Properties of Commission I.2 of the International Union of Pure and Applied Chemistry) has undertaken the responsibility of examining other liquids for use as viscosity reference fluids. Thus, in addition to the recommended values for the viscosity of water, values for the viscosity of *n*-hexane, *n*-heptane, *n*-octane, *n*-decane, *n*-dodecane, and *n*-tetradecane[2] at various temperatures and at atmospheric pressure were also recommended.

At higher pressures, Assael *et al.*[1, 3] and Santos *et al.*[4] have proposed reference correlations for the viscosity of toluene and cyclopentane, primarily for low temperatures. The original correlation for toluene, proposed by Assael *et al.*[1] covers the temperature interval from 213 to 373 K and the pressure range from 0.1 to 250 MPa. In the second paper, Santos *et al.*[4] proposed a reference correlation for toluene along the saturation line from 260 to 400 K. For cyclopentane, Assael *et al.*[3] published a reference correlation for the viscosity as a function of temperature and density valid from 220 to 310 K for pressures up to 25 MPa. Under these conditions, the viscosity of toluene ranges from 0.2 to 3.0 mPa s and the viscosity of cyclopentane from 0.4 to 1.5 mPa s.

The viscosities of these fluids are very much lower than those of the common mineral, synthetic and vegetable oils used in industry, as well as those of the different crudes found in oil reservoirs. Oil exploration increasingly involves reservoirs at temperature and pressures not previously exploited, and the viscosity is an extremely important parameter necessary for the estimation of fluid mobility and hence well production rates, as well as for well testing and injection processes.[5] Unfortunately, there is a scarcity of literature data for reference fluids of moderate viscosity at high pressure that could be employed to perform calibrations under similar conditions to those in reservoirs for the viscosity ranges required by industry, or to verify the correct operation of high-pressure viscometers for such relatively viscous materials. Under the auspices of IATP, diisodecyl phthalate, DIDP, has been studied for this purpose, and a reference correlation of a limited temperature range (293 to 303 K) at 0.1 MPa, has been published.[6] Some laboratories have also published viscosity values of DIDP at higher pressures over a broader range of temperature.[7-12] However, the possible effect of known differences in the distribution of isomers found in different DIDP commercial samples on the viscosity remains open,[7, 13] and this could be a drawback. Furthermore, the prime manufacturer of high purity DIDP has discontinued production.

Other fluids that might be suitable candidates as moderate viscosity reference fluids, and that exist as single isomers, are squalane (SQN), di(2-ethylhexyl) sebacate (DEHS), 2-ethylhexyl benzoate (EHB), and bis(2-ethylhexyl) phthalate (DEHP). It should be pointed out that the European Chemical Agency has listed DEHP as a 'Substance of Very High Concern (SVHC)' (20th October 2008), classifying it as toxic to (human) reproduction.[11, 14] Consequently, this substance may not meet occupational safety and health (OSH) criteria in certain countries or organizations for use as a viscosity reference fluid.[11, 13] Of the remaining compounds, EHB is quite an expensive material and has the lowest viscosity. DEHS has an important advantage in that it is a common material, being used as a power transmitting fluid, but its main drawback is that it is only available with 98% purity at present.

Hence, in this paper, we have focused our attention on squalane, SQN ($C_{30}H_{62}$, 2,6,10,15,19,23-hexamethyltetracosane). Its advantages are that it is chemically stable over a wide temperature range, has a low vapor pressure, is relatively inexpensive, and is available with mole purities above 99%. The only drawback is that it is less viscous than DIDP and DEHS, though more so than DEHS and EHB. There is, as yet, no overall, reliable correlation of the literature viscosity data for SQN for broad temperature and pressure ranges, though an attempt has recently been made by Polishuk.[15] He has considered both viscosity-residual entropy and friction-theory approaches coupled with the use of SAFT equations of state, as well as a modified Yarranton−Satyro correlation but found unsatisfactory accuracy for SQN with these models.

In this work we propose for the first time a reference correlation for the viscosity of squalane at 0.1 MPa. Although this correlation does not extend to higher pressures, it is a necessary first step in establishing high-viscosity reference values. The correlation is based on a series of new viscosity measurements carried out specifically for this reason, as well as an existing set of previously reported measurements. Hence for this work, we have accurately measured the viscosity of SQN as a function of temperature using capillary, falling body, quartz-crystal resonator, rotating cylinder, and vibrating-wire viscometers in four different laboratories at the Universities of New South Wales (UNSW), Pau (UPPA), Santiago de Compostela (USC), and Aristotle University of Thessaloniki (AUTh).

In order to develop the reference correlation, a prerequisite is the critical assessment of the available experimental data. For this purpose, two categories of experimental data are defined: primary data employed in the development of the correlation, and secondary data used simply for comparison purposes. According to the recommendation adopted by IATP, the primary data are identified by a well-established set of criteria.[16] These criteria have been successfully employed to establish standard reference values for the viscosity and thermal conductivity of fluids over wide ranges of conditions, with uncertainties in the range of 1%. However, in many cases, such a narrow definition unacceptably limits the range of the data representation. Consequently, within the primary data set, it is also necessary to include results that extend over a wide range of conditions, albeit with a poorer accuracy, provided they are consistent with other more accurate data or with theory. In all cases, the accuracy claimed for the final recommended data must reflect the estimated uncertainty in the primary information.

2. New Measurements

As already discussed, new measurements of the viscosity of squalane as a function of the temperature at 0.1 MPa, were carried out for this work at four laboratories, with five different instruments. The squalane samples (CAS 111-01-03) employed in the laboratories of UNSW, UPPA and USC, were all obtained from Sigma-Aldrich, with manufacturer's purity given as better than 99.0% by gas chromatographic analysis, and with a water content of 12×10^{-6} weight fraction determined by Karl Fischer analysis. The squalane sample employed at AUTh, was obtained from Merck, with manufacturer's purity given as better than 99.0% by gas chromatographic analysis. In all cases, no further purification was carried out. The results of the viscosity measurements in each laboratory are shown in Table 1. The equipment employed and their uncertainty is briefly discussed in the following four sections.

2.1. Measurements at UNSW

A falling-body viscometer, described previously,[17, 18] was employed for the viscosity measurements at the University of New South Wales. The reproducibility of the instrument was found to be 1%. The viscometer constant was determined by calibration with Cannon Instrument Company oils, as described previously,[11] at atmospheric pressure between 313.15 and 363.15 K. The estimated uncertainty of the viscosity measurements performed with this viscometer and this procedure is 2 %.

2.2. Measurements at UPPA

Two viscometers were employed at the University of Pau. One set of measurements was taken from 278.15 to 348.15 K with an Ubbelohde capillary viscometer, connected to an automatic AVS350 Schott Geräte Analyzer. The temperature of the fluid was controlled within 0.05 K (AOIP PHP602) using a thermostatic bath. The dynamic viscosity is obtained from the product of the kinematic viscosity and the density[19] with an uncertainty of less than 1%. Each capillary tube is provided with a calibration certificate but the calibration of the capillary viscometer was checked at several temperatures using "Viscosity Reference Standard" fluid S20 provided by Cole-Parmer.

The second set of measurements was carried out in a quartz-crystal resonator viscometer, recently developed by Daridon *et al.*[20] The sensor is a highly polished quartz crystal which has a nominal frequency of 3 MHz. It is fixed into a variable-volume cell that operates at up to 80 MPa (this paper refers to only 0.1 MPa). A heat-carrying liquid is circulated around the cell from a thermostat bath circulator (Haake F6) which has a stability of 0.01 K. A platinum resistance thermometer inserted into the vessel is used to measure the temperature of the cell with an uncertainty of 0.1 K. In this technique, the viscosity is determined by measuring the damping of the quartz vibrations for different overtones. The coefficient related to the quartz surface morphology,[21] is determined by calibration for each quartz crystal, using a *n*-decane. The estimated uncertainty of the measurements was found to be ± 2%.

2.3. Measurements at USC

At the University of Santiago de Compostela, an Anton Paar SVM3000 rotating-cylinder viscometer (Stabinger type), already described elsewhere,[22] was used for the measurements of the viscosity from 278.15 to 373.15 K at atmospheric pressure. The SVM 3000 uses Peltier elements for fast and efficient thermal equilibration. The temperature uncertainty is 0.02 K from 288.15 to 378.15 K and 0.05 K outside this range. The uncertainty of the viscosity was 1%, and this was verified using two reference fluids from the Cannon Instrument Co., S60 and N100; deviations from the reference data being less than 1%.

2.4. Measurements at AUTh

Measurements at the Laboratory of Thermophysical Properties & Environmental Processes, at the Aristotle University of Thessaloniki, were carried out in a recently developed vibrating-wire viscometer.[12] A 300 micron diameter tungsten wire was employed and the absolute uncertainty was calculated to be 1%.

3. The Correlation

Table 2 summarizes, to the best of our knowledge, the present measurements and the experimental measurements[11,23-38] of the viscosity of squalane as a function of the temperature at 0.1 MPa. 22 sets are included in the table. From these sets, six were considered as primary data. These consist of the new five sets taken during the course of this work, employing the best possible practices in order to maintain a very low uncertainty. Additionally, the earlier measurements of Harris,[11] carried out ~~in~~ with a falling-body viscometer were also included in the primary data set.

The remaining sets were considered secondary, as they show higher uncertainty, or do not include purity information, or present only one measurement at room temperature. Also literature kinematic viscosity measurements that lack the corresponding densities, are excluded from the primary data set. The measurements of Deegan *et al.*[31] (169 - 253 K) were not included in the primary data set, as they lie outside the temperature range covered by other investigators, and can not be readily validated. Furthermore, no information on uncertainty or purity was given. Finally, we note that Ciotta *et al.*[19] have carried out measurements of the viscosity of squalane as a function of pressure along four isotherms but their measurements started from high pressures that do not allow accurate extrapolation to 0.1 MPa.

The primary data, weighted according to their uncertainty, were fitted to an equation for the viscosity, η in mPa s, as a function of the absolute temperature, T in K, as

$$\eta = 0.06266 \exp\left(\frac{808}{T - 165.9}\right), \qquad (1)$$

This equation represents the selected primary data at 0.1 MPa, from 273 K to 373 K. The percentage deviations of the experimental values from the values calculated by Eq.(1), are shown in Figure 1.

Table 3 summarizes comparisons of the primary data with the correlation. We have defined the percent deviation as PCTDEV = $100(\eta_{\mathrm{exp}} - \eta_{\mathrm{fit}})/\eta_{\mathrm{fit}}$, where η_{exp} is the experimental value of the viscosity and η_{fit} is the value calculated from the correlation. Thus, the average absolute percent deviation (AAD) is found with the expression AAD = $(\sum|\mathrm{PCTDEV}|)/n$, where the summation is over all n points, the bias percent is found with the expression BIAS = (∑PCTDEV)/*n*. The average absolute percentage deviation of the fit is 0.67, the bias -0.12, and the expanded uncertainty, with a coverage factor $k = 2$, is 1.5%.

Figure 2 shows the percentage deviations of all secondary viscosity data from the values calculated from Eq. (1), as a function of temperature at 0.1 MPa. Two sets are not included in the figure; the measurements of Sautermeister and Priest,[23] taken from a very small logarithmic diagram which show deviations of more than 20%, and the measurements of Deegan *et al.*[31] which lie outside the temperature range of this correlation. The majority of the remaining deviations are within 3-5% of the present correlation. It is also worth mentioning, that in 1957, Sax and Stross[38] proposed a value of the kinematic viscosity of squalane at 310.93 K, as a standard value. It can be seen that, if converted to dynamic viscosity, this value is very close (about 1%) to the present correlation.

Table 4 lists typical values of the viscosity of squalane calculated by Eq. (1) as a function of temperature at 0.1 MPa.

4. Conclusion

A new correlation for the viscosity of squalane has been developed. The correlation should be valuable as it is the first to cover a moderately high viscosity range 3 to 118 mPa s. It is based on new viscosity measurements carried out for this work, as well as other critically evaluated experimental data. The correlation is valid from 273 K to 373 K at 0.1 MPa. The average absolute percentage deviation of the fit is 0.67, and the expanded uncertainty, with a coverage factor $k = 2$, is 1.5%.

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TABLE 1. New viscosity measurements of squalane at 0.1 MPa.

AUTh		UPPA-C		UPPA-QCR		USC		UNSW	
T (K)	η (mPa s)	T (K)	η (mPa s)	T (K)	η (mPa s)	T (K)	η (mPa s)	T (K)	η (mPa s)

283.77	60.20	278.15	83.95	293.15	35.60	278.15	83.90	313.15	15.07
288.47	46.10	283.15	61.83	303.15	22.10	283.15	61.84	338.15	6.72
293.29	35.59	288.15	46.34	313.15	14.70	288.15	46.74	348.15	5.21
298.12	27.95	293.15	36.04	323.15	10.60	293.15	36.06	363.15	3.72
303.07	22.45	303.15	22.53	333.15	7.70	298.15	28.33	363.15	3.72
308.09	18.36	323.15	10.63			303.15	22.66		
313.13	15.00	348.15	5.33			308.15	18.40		
318.17	12.56					313.15	15.16		
323.19	10.57					318.15	12.66		
328.26	8.99					323.15	10.69		
333.20	7.80					328.15	9.13		
338.18	6.81					333.15	7.87		
343.07	6.00					338.15	6.85		
348.08	5.32					343.15	6.01		
353.08	4.72					348.15	5.31		
358.13	4.20					353.15	4.72		
362.98	3.78					358.15	4.23		
						363.15	3.81		
						368.15	3.45		
						373.15	3.13		

TABLE 2. Viscosity measurements of squalane at 0.1 MPa.

1st author	Year published	Technique employed[a]	Purity[b] (%)	Uncertainty (%)	No. of data	Temperature Range (K)
Primary Data						

AUTh[c]	2013	VW	99.0	1.0	17	283-363
UPPA[c]	2013	C	99.0	1.0	7	278-348
UPPA[c]	2013	QCR	99.0	2.0	5	293-333
USC[c]	2013	RC	99.0	1.0	20	278-373
UNSW[c]	2013	FB	99.0	2.0	5	313-363
Harris[11]	2009	FB	99.0	2.0	40	273-353
Secondary Data						
Sautermeister[23]	2012	RB	99.0	3.0	4	293-423
Hata[24]	2010	RB	na	na	3	313-423
Dubey[25]	2008	C	99.0	na	3	298-308
Bair[26]	2006	RB	99.0	na	4	293-373
Kumagai[27]	2006	FB	98.0	2.9	4	273-333
Pensado[28]	2006	RB	99.0	1.5	6	303-353
Tripathi[29]	2005	C	99.0	0.9	1	298
Bair[30]	2002	FB	na	na	3	303-373
Deegan[31]	1999	RB	na	na	11	169-253
Fermeglia[32]	1999	C	99.0	1.0	1	298
Kumagai[33]	1995	C	99.0	1.7	4	273-333
Krahn[34]	1994	RB	99.0	2.0	3	298-453
Jambon[35]	1977	C	na	na	1	298
Barlow[36]	1972	C	GC	0.5	10	243-311
Kuss[37]	1972	FB	na	1.3	4	298-353
Sax[38]	1957	C	99.9	na	1	311

[a] C, Capillary; FB, Falling Body; QCR, Quartz Crystal Resonator; RB, Rolling Body; RC, Rotating Cylinder; VW, Vibrating Wire.

[b] GC, Gas Chromatography purity grade; na, not available.

[c] Present work.

TABLE 3. Evaluation of the squalane viscosity correlation for the primary data.

1st Author	Year Publ.	AAD (%)	BIAS (%)
AUTh[a]	2013	0.60	-0.18
UPPA[a,b]	2013	0.43	0.14
UPPA[a,c]	2013	1.69	-1.69
USC[a]	2013	0.51	0.51
UNSW[a]	2013	1.16	-1.16
Harris[11]	2009	0.62	-0.13
Entire data set		**0.67**	**-0.12**

[a] Present work, [b] Capillary, [c] Quartz-crystal viscometer

TABLE 4. Values Calculated by Eq. (1)

T (K)	η (mPa s)
273.00	118
283.00	62.2
293.00	36.1
303.00	22.7
313.00	15.2
323.00	10.7
333.00	7.89
343.00	6.00
353.00	4.70
363.00	3.78
373.00	3.10

Figure Captions

1. Percentage deviations of the viscosity primary data as a function of the temperature at 0.1 MPa, from the values calculated by Eq. (1). AUTh (●), UPPA C (△), UPPA QCR (▲), USC (◆), UNSW (■), Harris[11] (□).

2. Percentage deviations of the viscosity secondary data as a function of the temperature at 0.1 MPa, from the values calculated by Eq. (1). Hata and Tamoto[24] (⧋), Dubey and Sharma[25] (✳), Bair[26] (△), Kumagai *et al.* [27] (■), Pensado *et al.*[28] (□), Tripathi[29] (◆), Bair *et al.*[30] (◑), Fermeglia and Torriano[32] (◇), Kumagai and Takahashi[33] (▲), Krahn and Luft[34] (+), Jambon and Delmas[35] (×), Barlow and Erginsav[36] (○), Kuss and Golly[37] (●), Sax and Stross[38] (⊕).