

## IUPAC Technical Report

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# International Standard for viscosity at temperatures up to 473 K and pressures below 200 MPa (IUPAC Technical Report)

<https://doi.org/10.1515/pac-2018-0202>

Received February 06, 2018; accepted July 23, 2018

**Abstract:** This paper presents the results of an investigation into possible liquid viscosity standards to meet an industrial requirement for a liquid with a nominal viscosity of 20 mPa s at a temperature of 473 K and pressure of 200 MPa with a relative expanded uncertainty of less than 5%. There are no commercially available certified viscosity reference liquids that meet this requirement. Four candidate fluids were examined: squalane, Krytox GPL102, tris(2-ethylhexyl) trimellitate (TOTM), and dipentaerythritol hexa(3,5,5-trimethylhexanoate) (DiPEiC<sub>9</sub>). Although none of these fluids satisfies all of the criteria, two fluids were identified as being suitable as International Standards for viscosity at temperatures up to 473 K and pressures below 200 MPa. These fluids are squalane and tris(2-ethylhexyl) trimellitate (TOTM), which at  $T=473.15$  K and  $p=200$  MPa present viscosity values of 5 mPa s and 10 mPa s, respectively.

**Keywords:** DiPEiC<sub>9</sub>; high-viscosity standard; Krytox GPL102; squalane; TOTM.

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**Article note:** Sponsoring body: IUPAC Physical and Biophysical Chemistry Division and the International Association for Transport Properties (IATP).

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## 1 Introduction

In 2012, there were two independent projects attempting to identify a viscosity standard for liquids at a nominal value of about 20 mPa s at temperatures up to 473 K and pressure up to 200 MPa: one in Europe and the other in North America. The interest in a standard reference fluid for viscosity at high temperatures and high pressure was due to the trend within the oil industry toward the exploitation of deeper hydrocarbon reserves, both on- or off-shore, characterized by temperatures up to 473 K and pressures up to 200 MPa. One of the original aims of this project was to link these otherwise independent activities and to provide a single international standard. The project has involved 14 research groups from academia and one company (Schlumberger) working towards this end:

### European research groups

- Lisbon group (Prof. João Fareleira and Dr. Fernando Caetano) University of Lisbon, Portugal
- London group (Prof. Sir William Wakeham and Prof. J.P. Martin Trusler) Imperial College London, UK
- Thessaloniki group (Prof. Marc J. Assael and Dr. Sofia Mylona) Aristotle University of Thessaloniki, Greece
- Pau group (Prof. Jean Luc Daridon, Prof. Guillaume Galliero and Prof. Christian Boned) University of Pau, France
- Santiago de Compostela group (Prof. Josefa Fernandez and Dr. María J. P. Comuñas) University of Santiago de Compostela, Spain

### American research groups

- Pittsburgh group 1 (Prof. Robert M. Enick) University of Pittsburgh, PA, USA
- Pittsburgh group 2 (Dr. Baled and Dr. Tapriyal) National Energy Technology Laboratory, PA, USA
- Richmond group (Prof. Mark McHugh) Virginia Commonwealth University, VA, USA
- Atlanta group (Dr. Scott Bair) Georgia Institute of Technology, Atlanta, GA, USA
- Boulder group (Dr. Arno Laesecke) National Institute of Standards and Technology: NIST, CO

### Australian research groups

- Canberra group (Dr. Kenneth R. Harris) University of New South Wales
- Perth group (Prof. Eric May and Prof. Kenneth N. Marsh), University of Western Australia
- Industrial groups
- Abingdon group (Dr. Kurt A. G. Schmidt) Abingdon Technology Center, Schlumberger, UK
- Sugar Land group (Dr. A. R. H. Goodwin, who sadly passed away during the project) Schlumberger Technology Center, TX, USA

The industrial requirement is a viscosity standard for a liquid with a nominal value of 20 mPa s at a temperature of 473 K and pressure of 200 MPa and a relative expanded uncertainty less than 5%. The target viscosity value is representative of light oils found in ultra-deep formations beneath the deep waters of the Gulf of Mexico. Initial specifications were initially established as 200 mPa s at 534.15 K and 241 MPa during the HTHP Workshop initiated by Schlumberger and Cambridge Viscosity, Inc. on January 22, 2010 [1, 2], but the difficulty in attaining these conditions experimentally resulted in a reduction of the viscosity, temperature, and pressure of these specifications.

Other features normally expected of a standard reference material, such as low toxicity, ready availability, and uniformity from lot to lot from a manufacturer, are also necessary. The viscosity and density must be known over a range of temperatures and pressures. At present, there are no commercially available certified

**Table 1:** Compounds studied in this project.

Fluid	$\eta(293.15 \text{ K}, 0.1 \text{ MPa})/\text{mPa s}$	$\eta(473.15 \text{ K}, 200 \text{ MPa})/\text{mPa s}$
1. Squalane	36	5
2. Krytox GPL 102	63	25
3. Tris(2-ethylhexyl) trimellitate, TOTM	240	10
4. Dipentaerythritol hexa(3,5,5-trimethylhexanoate), DiPEiC <sub>9</sub>	2077	80

viscosity reference liquids that fulfil this requirement. We searched mainly for appropriate standard reference viscosities for the selected fluids, but also for appropriate standard reference fluids. In this project, we examined four candidate fluids, as listed in Table 1. For the selection of these compounds, we used the previous work performed by the members of the consortium. In 2006, Bair [3] proposed squalane as a reference liquid for quantitative elastohydrodynamics, for which viscosity data at very high pressures (up to around 1 GPa) are needed. In 2007, Harris and Bair [4] indicated that squalane is a suitable candidate material for use as high-viscosity calibrants. Krytox oils were identified as possible candidates for the viscosity standard by the Working Group on High-Temperature, High-Pressure Viscosity Standards, which was created in 2009 in the framework of the International Association of Transport Properties (IATP) [5]. When the viscosity specifications were identified as 20 mPa s at a temperature of 473 K and pressure of 200 MPa, Krytox 102 was selected by Baled *et al.* [2]. Tris(2-ethylhexyl) trimellitate (TOTM) was proposed during this IUPAC project by Prof. Fareleira and collaborators [6, 7]. Dipentaerythritol hexa(3,5,5-trimethylhexanoate) was proposed by Comuñas *et al.* [8] as a potential candidate for more extreme viscosity conditions in the 9th meeting of the IATP in Boulder, Colorado.

## 2 Squalane

Squalane (2, 6, 10, 15, 19, 23-hexamethyltetracosane, CAS 111-01-3) is considered an interim solution because it is a relatively inexpensive material available from major chemical suppliers (e.g. Fluka and Sigma Aldrich) with mass-fraction chemical purities of at least 99 %. It is chemically stable over a wide temperature range and has a low vapor pressure, but its dynamic viscosity at  $T=473.15 \text{ K}$  and  $p=200 \text{ MPa}$  is around 5 mPa s, considerably lower than the target value of 20 mPa s. As a pure fluid of moderate viscosity, it may serve as an interim standard until other suitable reference fluids with higher viscosities can be identified and characterised.

### 2.1 Reference correlations

#### 2.1.1 2013 Atmospheric-pressure reference correlation

In 2013, under the auspices of the IATP, the Thessaloniki, Pau, Santiago, and Canberra groups reported a new reference correlation for the viscosity of squalane at 0.1 MPa [9], given by

$$\eta/(\text{mPa} \cdot \text{s}) = 0.06266 \exp\left(\frac{808}{T/\text{K} - 165.9}\right) \quad (1)$$

This correlation, valid at  $273 \leq T/\text{K} \leq 373$  and  $p=0.1 \text{ MPa}$ , was the first to cover a moderately high viscosity range, approximately 3 to 118 mPa s. It is based on critically-evaluated experimental viscosity data from the literature, but also includes new viscosity values measured with vibrating wire (VW), capillary (C), falling body (FB), quartz crystal resonator (QCR), and rotating cylinder (RC) viscometers. This was published in a correlation article [9]. The average absolute relative deviation of the fit is 0.67 % and the relative expanded uncertainty, with a coverage factor  $k=2$ , is 1.5 %.

### 2.1.2 2014 High-pressure reference correlation

In 2014, the Pau, Santiago de Compostela, and Canberra groups reported new viscosity data for squalane: 220 experimental viscosities obtained at temperatures between 293.15 K and 363.15 K and at pressures up to 350 MPa [10]. These data were measured with four different falling-body viscometers, a new quartz crystal resonator viscometer, a capillary viscometer, and a rotating cylinder viscometer. Comuñas *et al.* [10] used these measurements to provide a modified correlation as follows:

$$\eta/(\text{mPa} \cdot \text{s}) = A \exp\left(a_1 \Delta p + a_2 \Delta p^2 + \frac{b_0 + b_1 \Delta p + b_2 \Delta p^2 + b_3 \Delta p^3}{T/\text{K} - C}\right), \quad (2)$$

where  $\Delta p = p - p_{\text{ref}}$  and  $p_{\text{ref}} = 0.1$  MPa. The parameters  $A$ ,  $b_0$  and  $C$  were taken from eq. (1) ( $A = 0.06266$ ,  $b_0 = 808$  and  $C = 165.9$ ), while the other parameters are  $a_1 = 1.04106 \cdot 10^{-3} \text{ MPa}^{-1}$ ,  $a_2 = -2.31600 \cdot 10^{-6} \text{ MPa}^{-2}$ ,  $b_1 = 2.81118 \text{ MPa}^{-1}$ ,  $b_2 = -3.16018 \cdot 10^{-3} \text{ MPa}^{-2}$ , and  $b_3 = 3.29849 \cdot 10^{-6} \text{ MPa}^{-3}$ . In total, 176 data points were considered, at temperatures between 293.15 K and 363.15 K and at pressures up to 350 MPa, covering a viscosity range from 4.4 mPa s to 745 mPa s. The correlation fits the data with an absolute average relative deviation (AARD) of 1.5 %.

Mylona *et al.* [11] provided new reference correlations for the density and viscosity of squalane at high pressure. These correlations were based on critically evaluated experimental data taken from the literature. In the case of density, the correlation, based on the Tait equation [12], is valid from 273 K to 473 K at pressures to 200 MPa and is given by

$$\frac{\rho - \rho_0}{\rho} = C \log_{10}\left(\frac{B + p}{B + p_0}\right) \quad (3)$$

where  $C = 0.2$ ,  $p_0 = 0.1$  MPa, and  $B$  and  $\rho_0$  are given by

$$B/\text{MPa} = 398.314 - 1.25406(T/\text{K}) + 10.6525 \times 10^{-4}(T/\text{K})^2 \quad (4)$$

$$\rho_0 / (\text{kg} \cdot \text{m}^{-3}) = 996.28 - 0.6402(T/\text{K}) \quad (5)$$

This correlation has an AARD of 0.05 % and a relative expanded uncertainty at the 95 % confidence of 0.18 %.

Two viscosity correlations were developed by Mylona *et al.* [11]. The first of these, based on the Assael-Dymond model, is a function of density and temperature that is valid at temperatures from 320 K to 473 K and at pressures up to 200 MPa. This reference correlation is expressed as follows:

$$\eta = \frac{5}{16(2N_A)^{1/3} V_m^{2/3}} \left(\frac{MRT}{\pi}\right)^{1/2} \eta^*, \quad (6)$$

where  $N_A$  is the Avogadro constant,  $M$  is the molar mass,  $R$  is the universal gas constant,  $T$  is the temperature, and  $V_m$  is the molar volume (obtained from the density via equations 3 to 5). The reduced dimensionless viscosity,  $\eta^*$  is given by

$$\log_{10} \eta^* = -23274.3831 - 21623.6741 \Psi - 6698.8037 \Psi^2 - 692.0224 \Psi^3 \quad (7)$$

where the quantity  $\Psi$  is defined through the equation

$$\Psi = \log_{10}(V_m / V_0) \quad (8)$$

Here,  $V_0$  is a characteristic molar volume determined from the following function:

$$\log_{10}[V_0 / (\text{m}^3 \cdot \text{mol}^{-1})] = 0.308862 - 1.538769 \times 10^{-3}(T/K) + 2.712304 \times 10^{-6}(T/K)^2 - 1.774377 \times 10^{-9}(T/K)^3 \quad (9)$$

The AARD of this correlation is 1.4 % and the relative expanded uncertainty at 95 % probability is 3 %.

The second correlation is based on a modified Vogel-Fulcher-Tammann (VFT) equation [13–15] given by equation (2). The coefficient values are  $A = 0.0831311$ ,  $b_0 = 727.325$ ,  $C = 172.993$ ,  $a_1 = 2.06832 \cdot 10^{-3} \text{ MPa}^{-1}$ ,  $a_2 = -1.31522 \cdot 10^{-6} \text{ MPa}^{-2}$ ,  $b_1 = 2.60294 \text{ MPa}^{-1}$ ,  $b_2 = -4.19779 \cdot 10^{-3} \text{ MPa}^{-2}$ , and  $b_3 = 6.10051 \cdot 10^{-6} \text{ MPa}^{-3}$ . This correlation covers a broader temperature range, from 278 K to 473 K, at pressures up to 200 MPa, and has an AARD of 1.7 %. This correlation is slightly superior to that defined by eqs. (6–9) at low temperatures, while the opposite is true at temperatures higher than 410 K. Some selected reference viscosity values at different pressures and temperature conditions are conveniently tabulated by Mylona *et al.* [11].

## 2.2 Measurements after 2014

In 2015, Schmidt *et al.* [16] reported new experimental data and reference models for the viscosity and density of squalane. It is important to emphasize that these new density and viscosity values had already been used in the correlations of Mylona *et al.* [11]. For the density correlation, Schmidt *et al.* [16] used a Tait-like equation in the form of equation (3), with  $C = 0.200$  and  $B$  and  $\rho_0$  given as follows:

$$B/\text{MPa} = 382.2 - 1.162(T/K) + 9.305 \times 10^{-4}(T/K)^2 \quad (10)$$

$$\rho_0 / (\text{kg} \cdot \text{m}^{-3}) = 978.9 - 0.5355(T/K) - 1.571 \times 10^{-4}(T/K)^2 \quad (11)$$

The authors used a database that contained experimental density values within the temperature range from 273.15 to 524.70 K and the pressure range from 0.098 to 202.09 MPa. After applying a regression model, Schmidt *et al.* [16] rejected 64 density points. The AARD obtained by excluding the rejected points is 0.04 %. Based on the rejected data, the authors limited the use of this density model to pressures from 0.1 to 202.1 MPa and temperatures from 273 to 525 K.

For the viscosity reference model, Schmidt *et al.* [16] used the Comuñas *et al.* [17] equation

$$\eta(p, T) = A \exp\left(\frac{b_0}{T-C}\right) \left(\frac{p+E}{p_0+E}\right)^D \quad (12)$$

where  $A = 0.07610 \text{ mPa s}$ ,  $b_0 = 752.8 \text{ K}$ ,  $C = 170.7 \text{ K}$  and  $D$  and  $E$  are given as function of temperature by

$$D = -4.488 + 3330(T/K) + 1.736 \times 10^5(T/K)^2 \quad (13)$$

$$E/\text{MPa} = -468.4 + 5.072(T/K) - 7.421 \times 10^{-3}(T/K)^2 \quad (14)$$

In the case of viscosity, the authors used a database which contained experimental values in the temperature range from 242.70 to 473.07 K and the pressure range from 0.098 to 467 MPa. After again applying a regression model, Schmidt *et al.* [16] rejected 97 viscosity points. The AARD obtained by excluding the rejected points is 1.4 %. Based on the rejected data, the authors limited the use of their viscosity model to pressures from 0.1 to 467.0 MPa and temperatures from 273 to 473 K.

Bair [18] made a comment on the work of Schmidt *et al.* [16], indicating that their model cannot be used to analyze the consistency of the experimental viscosity data measured above 400 MPa because it is not able to correctly describe the change of the slope of the isothermal viscosity-pressure curve. Instead, Bair [18] proposed the use of a hybrid model to better describe the inflection point of the viscosity-pressure isotherms. In response, Schmidt *et al.* [19] suggested the following hybrid model:

$$\begin{aligned}
 p < p_0 & \quad \eta = \eta_{\text{ref}}(p, T) \\
 p > p_0 & \quad \eta = \eta_{\text{ref}}(p, T) \exp\left(\frac{C_f p}{p_\infty(T) - p} - \frac{C_f p_0}{p_\infty(T) - p_0}\right)
 \end{aligned}
 \tag{15}$$

where  $\eta_{\text{ref}}(p, T)$  is the viscosity given by the model described by the equations (12–14), the crossover pressure  $p_0$  is 467 MPa,  $C_f$  is the fragility parameter, and  $p_\infty(T)$  is the pressure for unbounded viscosity. The latter is given as a function of temperature by

$$p_\infty = p_a T + p_b, \tag{16}$$

where  $p_a$  and  $p_b$  are fitted parameters. From the correlation of 38 experimental viscosity data points of Bair [3, 20] in the temperature range 293.15 to 373.15 K and at pressures from 467 MPa to 1298 MPa, Schmidt *et al.* [19] obtained  $C_f = 2.2664$ ,  $p_a = 12.242 \text{ MPa K}^{-1}$ , and  $p_b = -1783.8 \text{ MPa}$ . The AARD obtained was 5.5 %.

Recently, new glass transition temperature data at pressures up to 0.8 GPa obtained by the transient hot-wire method and six new ultrahigh viscosity values at pressures from (1.00 to 1.35) GPa have been published by Bair *et al.* [21]. These authors present a correlation model of their data together with those of reference [3] based on the following equations:

$$\eta = \eta_g \exp\left\{\frac{-2.303C_1(T - T_g)F}{C_2 + (T - T_g)F}\right\} \tag{17}$$

where

$$T_g = T_g^0 + A_1 \ln(1 + A_2 p) \tag{18}$$

$$F = (1 + b_1 p)^{b_2} \tag{19}$$

The range of temperature of the correlation is from 293.15 K to 333.15 K, for pressures up to 1350 MPa. The values of the coefficients are given in Table 2.

For squalane, outside the temperature range 278 to 473 K and for pressures higher than 200 MPa there are no reference correlations. In our opinion, the Schmidt *et al.* [16] correlation is the most appropriate for pressures higher than 200 MPa and lower than 467 MPa. In the range 293.15 to 333.15 K, for pressures from 467 MPa up to 1350 MPa, the Bair *et al.* [21] equations should be used. Finally, from 333.15 to 373.15 K and at pressures from 467 MPa to 1298 MPa the hybrid model proposed by Schmidt *et al.* [19] can be used. Deviation plots can be found in the original articles for the reference correlations [9, 11] and that of Schmidt *et al.* [16]. Some selected reference density and viscosity values for squalane were provided by Comuñas *et al.* [9] and Mylona *et al.* [11].

The rheological behaviour of squalane has been studied by Bair [20, 22] at pressures up to 955 MPa and shear rates of up to  $10^4 \text{ s}^{-1}$ . This author has shown that squalane presents Newtonian behaviour at 293.15 K up to at least  $10^4 \text{ s}^{-1}$  at 636 MPa. This compound also behaves as Newtonian at shear stress lower than 5 MPa [22]. At lower pressures and/or higher temperatures it is expected that Newtonian behaviour occurs at even higher shear rates [23]. Viscoelastic effects are therefore not expected in normal high-pressure viscometer measurements, because the stress is low and there are no fast transients.

**Table 2:** Parameter values for equations (17–19) as reported by Bair *et al.* [21] and relative standard deviation  $s$ .

$\eta_g/\text{Pa s}$	$T_{g0}/\text{K}$	$A_1/\text{K}$	$A_2/\text{GPa}^{-1}$	$b_1/\text{GPa}^{-1}$	$b_2$	$C_1$	$C_2/\text{K}$	$s$
$1.23 \times 10^7$	184.46	263.8	0.3527	13.73	-0.3426	11.66	39.17	9.2 %



### 3 Krytox GPL102

Perfluoropolyethers (PFPEs) have been used as lubricants at extreme temperatures since 1960. The chemical formulation and physical properties of these polymers, as well as their uses as lubricants, have been reviewed by Walter *et al.* [24]. Krytox GPL102 has been chosen in the framework of this project because its viscosity at  $T=473$  K and  $p=200$  MPa is close to the nominally required value of 20 mPa s (see Table 1). The other main advantages of this fluid are its extreme thermal and oxidative stability, low evaporative losses, high chemical stability, and very good cold flow properties [24, 25]. Krytox GPL102 thus satisfies many of the criteria for a HTHP viscosity reference liquid. The main disadvantage is that Krytox GPL102 (CAS 812693-47-43) is not a pure compound but a polydisperse mixture of perfluoropolyethers  $F[CF(CF_3)CF_2O]_nCF_2CF_3$  with  $n=9.528$  and a mean molar mass of  $1720$  g mol<sup>-1</sup>. The first viscosity measurements at high pressures were reported in 2013 by Baled *et al.* [2] in the temperature range 311 to 533 K and up to 245 MPa. For the same lot (L1537), Bamgbade *et al.* [26] reported in 2012 the densities at temperatures from 298 to 533 K at pressures up to 275 MPa.

#### 3.1 Round-robin experimental study

In order to eliminate any lot-to-lot variations in chemical composition, a round-robin study was performed by various laboratories in which the viscosities of the same lot of Krytox GPL 102 (DuPont, Wilmington, DE, USA) were measured. Distribution of the samples was performed by National Energy Technology Laboratory and University of Pittsburgh (Dr. Deepak Tapriyal and Prof. Robert Enick). The lot number is K2391, with a mean molar mass of  $1720$  g mol<sup>-1</sup>. The weight fraction of polyfluoroethers is 1, and the water content  $10^{-5}$ .

Fortin *et al.* [27] measured the density and the viscosity, at 0.1 MPa from 263.15 to 373.15 K, of six Krytox GPL oils among the two samples of GPL-102 (lots K1608 and K2391). Lot-to-lot deviations for density were well within reported experimental uncertainties in this work, whereas viscosity lot-to-lot deviations (from 7 % to 15 %) far exceeded estimated expanded uncertainties.

High pressure density measurements of this lot were performed by Comuñas *et al.* [28] from 278 to 398 K and up to 120 MPa, while relative volumes were measured by Bair [29] from 313 K to 423 K and up to 350 MPa. The densities obtained by both groups agree within the combined uncertainties of the densimeters. Nevertheless, the densities of the round-robin sample are significantly lower than those determined with another lot by Bamgbade *et al.* [26]. The difference between both data sets reaches values of 1.1 %, which is a big deviation for this property. Comuñas *et al.* [28] correlate their density values through a Tait-type equation given by

$$\frac{\rho - \rho_0}{\rho} = C' \ln \left( \frac{B + p}{B + p_0} \right) \quad (20)$$

where  $C' = 0.0769$ ,  $p_0 = 0.1$  MPa and  $B(T)$  and  $\rho_0$  are given by

$$B/\text{MPa} = 286.57 - 1.09314(T/\text{K}) + 1.0979 \times 10^{-3}(T/\text{K})^2 \quad (21)$$

$$\rho_0/(\text{g} \cdot \text{cm}^{-3}) = 2.3803 - 1.6480 \times 10^{-3}(T/\text{K}) - 0.3804 \times 10^{-6}(T/\text{K})^2 \quad (22)$$

This correlation covers a temperature range from 278 K to 398 K at pressures up to 120 MPa and has an AARD of 0.014 %.

Viscosity measurements at high pressures of the round robin sample were measured in the three European laboratories of the Universities of Pau, Thessaloniki, and Santiago de Compostela, in two American laboratories in Pittsburgh and Atlanta, and at UNSW Canberra in Australia. Table 3 gives a summary of these viscosity measurements.

Bair [29] and Harris [30] reported correlations of their viscosity data. Baled *et al.* [33] correlated their viscosity data with the following equation:

**Table 3:** Details of viscosity measurements performed with the round robin Krytox GPL102 sample.

First author	Technique	T range/K	Maximum p/MPa	Maximum $\eta$ /mPa s
Harris [30]	Falling body	273–368	225	4182
Bair [29]	Falling body	313–433	850	2 552 300
Mylona <i>et al.</i> [31]	Vibrating wire+ Couette	283–363	20	109
Bazile <i>et al.</i> [32] Un. Pau	Falling body+ Capillary	293–363	200	1850
Bazile <i>et al.</i> [32] Un. Santiago	Falling body+ Stabinger	278–363	150	2075
Baled <i>et al.</i> [33]	Rolling-ball	314–524	242	3288

$$\eta/(\text{mPa} \cdot \text{s}) = \exp \left\{ a + bp + cp^2 + \frac{d + ep + fp^2 + gp^3}{T - T_0} \right\} \quad (23)$$

The coefficient values are  $a = -2.3979$ ,  $b = 7.8397 \cdot 10^{-3} \text{ MPa}^{-1}$ ,  $c = -2.8990 \cdot 10^{-5} \text{ MPa}^{-2}$ ,  $d = 840.39 \text{ K}$ ,  $e = 4.6243 \text{ MPa}^{-1} \text{ K}$ ,  $f = -9.3370 \cdot 10^{-3} \text{ MPa}^{-2} \text{ K}$ ,  $g = 2.7080 \cdot 10^{-5} \text{ MPa}^{-3} \text{ K}$ , and  $T_0 = 164.24 \text{ K}$ . This correlation covers a temperature range from 314 and 527 K at pressures between 7 and 242 MPa and has an AARD of 1.35 %. The deviation between the values obtained from this correlation and the viscosity data of Bair [17] range from  $-0.95 \%$  to  $+8.9 \%$  and has an AARD of 3.6 %, with the worst deviations occurring at the highest temperature. Deviations from the data of Harris [30] range from  $-4.6 \%$  to  $+0.04 \%$ , with an AARD of 1.5 % and the worst deviations found at 323 K. The deviations from the viscosities of Mylona *et al.* [31] range from  $-0.11 \%$  to  $-3.5 \%$ , with an AARD of 2.5 %. Deviation plots can be found in the original articles [29, 30, 33]. The future use of the three individual correlations for the viscosity of Krytox 102 is not clear, because it is difficult to get identical samples.

Cantow *et al.* [34] have characterized the rheological behaviour at various temperatures of two perfluoropolyethers with the same chemical structure ( $\text{F}[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_n\text{CF}_2\text{CF}_3$ ) as Krytox 102, but with much higher mean molar masses ( $M_w = 9060 \text{ g mol}^{-1}$  and  $M_w = 16 800 \text{ g mol}^{-1}$ ). They found that both oils behave as Newtonian liquids at shear stress up to 1000 Pa at temperatures lower than 216 K. Wider ranges of Newtonian behaviour under higher shear stress can be expected for lower molecular Krytox oils, such as Krytox 102 ( $M_w = 1720 \text{ g mol}^{-1}$ ), as well as for higher temperatures. Non-Newtonian behaviour is therefore not expected under the conditions of high-pressure viscometers.

## 4 Tris(2-ethylhexyl) trimellitate, TOTM

Tris(2-ethylhexyl) benzene-1,2,4-tricarboxylate (CAS-No. 3319-31-1 and EC-No. 222-020-0) or tris(2-ethylhexyl) trimellitate (TOTM) was proposed as a reference material in 2014 by the Lisbon group [6, 7]. Trimellitate esters generally have a low vapor pressure, are liquid over a large temperature range, and have high viscosities; these characteristics make them suitable for specialty lubricants, as air compressors formulations, high temperature chain oils, or transformer/dielectric fluids, and as greases [35]. Trimellitates are now proving successful for temperatures up to 200 °C. Some manufacturers in the United States also market ester-based products as lubricants for high-temperature conveyor bearings, for use up to 280 °C [35]. TOTM is a pure compound whose normal freezing and boiling temperatures are 230 and 687 K, respectively [36], so it has a very wide liquid range. According to its material safety data sheet (MSDS) and European Directive 67/548/EEC, TOTM is classified as a nonhazardous substance, although it is noted that special care should be taken if it is swallowed, inhaled, or if it contacts the skin or eyes [36]. These characteristics indicate that TOTM is suitable as a standard reference material. In addition, Avelino *et al.* [37] performed tests with shear stresses up to 750 Pa and shear rates up to 4000  $\text{s}^{-1}$  under atmospheric pressure. The Newtonian character of liquid TOTM has been confirmed for shear rates up to 600  $\text{s}^{-1}$ . This confirms the suitability of TOTM as a standard reference fluid for the calibration of viscometers for the industrial purposes reported earlier.



## 4.1 Reference viscosity correlation

In 2017, Wakeham *et al.* [36] reported a reference correlation for TOTM based on the previous work of the nine groups of this project. For these measurements, four lots (MKBH8084V, MKBQ0304V, MKBT5164V, and MKBX3929V) of TOTM were used, all supplied by Sigma-Aldrich. The mass fraction purity of each of the four lots was higher than 0.99 g/g. Wakeham *et al.* [36] concluded that TOTM is thermally stable and can serve as a reference material at temperatures up to 473 K by exposing TOTM samples to this temperature for approximately 3 days at atmospheric pressure and then analyzing the sample. In addition, Baled *et al.* [33] found they could measure high-pressure viscosities consistently at temperatures as high as 523 K.

The densities of three of the lots of TOTM specified above were measured by Diogo *et al.* [6, 38], Avelino *et al.* [37], Bair [29], Bazile *et al.* [39], and Bamgbade *et al.* [40]. The overall range is from 293 to 523 K at pressures up to 350 MPa. In addition, Bazile *et al.* [39] have also measured the speed of sound at temperatures from 293 to 373 K at pressures up to 140 MPa, calculating the densities from these values. Wakeham *et al.* [36] employed equation (20) to correlate all the above density values from 293 to 523 K at pressures up to 250 MPa.

In this case,  $C' = 0.087455$ ,  $p_0 = 0.1$  MPa and  $B$  and  $\rho_0$  are given by

$$B/\text{MPa} = 370.982 - 0.60030(T/\text{K}) - 1.090579 \times 10^{-3}(T/\text{K})^2 + 1.9977 \times 10^{-6}(T/\text{K})^3 \quad (24)$$

$$\rho_0 / (\text{kg} \cdot \text{m}^{-3}) = 1207.540 - 0.758786(T/\text{K}) + 0.414842 \times 10^{-6}(T/\text{K})^2 \quad (25)$$

The root mean square relative deviation is 0.051 %.

Analyzing the densities of the different lots, Wakeham *et al.* [36] concluded that the variability of composition of samples among lots has an effect on the density within the uncertainty in the density measurements.

The viscosities of three of the lots of TOTM were measured by Diogo *et al.* [7, 38], Bair [29], Baled *et al.* [33], Assael *et al.* [41], and Liñeira del Río *et al.* [42]. The overall range of the experimental values is from 298 to 523 K at pressures up to 350 MPa. This reference correlation is expressed by equation (6), but in this case, the reduced dimensionless viscosity,  $\eta^*$ , is given by

$$\log_{10} \eta^* = 8.723136 - 54.986\Psi - 462.94\Psi^2 + 8.9429 \times 10^3 \Psi^3 - 4.7993 \times 10^4 \Psi^4 + 8.8238 \times 10^4 \Psi^5 \quad (26)$$

where the quantity  $\Psi$  is defined by eq. (8), with  $V_0$  being a characteristic volume given by

$$V_0 / (\text{cm}^3 \cdot \text{mol}^{-1}) = 462.4376 - 0.429149(T/\text{K} - 303.16) - 6.1968 \times 10^{-4}(T/\text{K} - 303.16)^2 \quad (27)$$

The above correlation scheme is proposed for the temperature range from 303 to 477 K, up to pressures of 200 MPa and viscosities of 1000 mPa s [36]. The relative expanded uncertainty of the viscosity results is estimated as 3.2% at a 95% confidence level. Deviation plots and an executable Excel file to interpolate the viscosity and density values for TOTM for any pairs of temperature and pressure within the corresponding ranges can be found in [36].

## 5 Dipentaerythritol hexa(3,5,5-trimethylhexanoate), DiPEiC<sub>6</sub>

[3-(3,5,5-trimethylhexanoyloxy)-2-[[3-(3,5,5-trimethylhexanoyloxy)-2,2-bis(3,5,5-trimethylhexanoyloxy-methyl)pro-poxy]methyl]-2-(3,5,5-trimethylhexanoyloxymethyl)propyl] 3,5,5-trimethylhexanoate) or dipentaerythritol hexa(3,5,5-trimethylhexanoate) (CAS No. 65870-97-5) is a stable ester that is used in the formulation of current synthetic lubricants but is more viscous than Krytox GPL102 and TOTM under the same conditions. This compound, with a viscosity of 2077 mPa s at  $T = 293.15$  K and  $p = 0.1$  MPa, was chosen to cover current needs for very viscous reference fluids in the fields of lubricants and oil extraction [8, 43].

The sample of dipentaerythritol hexa(3,5,5-trimethylhexanoate) used in this project was provided by Croda-Uniqema (UK) and was distributed by the Laboratory of Thermophysical Properties at the Applied Physics Department of the University of Santiago de Compostela to the Bair and Harris laboratories. Harris [30] measured the NMR spectra to confirm that there was no contamination by the parent alcohol and acid and to identify the chemical structure. The extremely low vapor pressures have been measured by Garcia *et al.* [44]. Heat capacities and thermal conductivities at  $p = 0.1$  MPa were measured by López *et al.* [45]

## 5.1 Density and viscosity measurements and correlations

Harris [30] has measured densities of DiPEiC<sub>9</sub> at  $p = 0.1$  MPa at temperatures from 273.15 to 363.15 K using a vibrating-tube densimeter. Bair and Yamaguchi [46] have reported pressure–relative volume–temperature values determined with a piezometer from at temperatures from 313.15 to 373.15 K at pressures up to 400 MPa with a relative uncertainty in the relative volume of 0.2%. López *et al.* [45] have reported experimental densities of DiPEiC<sub>9</sub> at temperatures between 283.15 and 398.15 K at pressures up to 70 MPa. All these values, which agree within the combined uncertainty, were used by López *et al.* [45] to make three correlations using two scaling EoS and the Tammann-Tait EoS (TT). The data covers a temperature range from 273.15 to 398.15 K, a density range from 895 to 1075 kg m<sup>-3</sup> and pressures from 0.1 to 400 MPa. The quality of the three correlations is similar. For simplicity, in this report we only describe the correlation based on TT EoS, which is as follows:

$$V = V_0 \left\{ 1 - C' \ln \left( \frac{B + p}{B + p_0} \right) \right\} \quad (28)$$

where  $C' = 0.084901$  and  $V_0$  is the specific volume at  $p = p_0$ ;  $V_0$  and  $B$  were given as functions of temperature by

$$V_0 / (\text{m}^3 \cdot \text{kg}^{-1}) = 1.02884 \times 10^{-3} + 7.224 \times 10^{-7} (T/\text{K} - 283.15) + 4.61 \times 10^{-10} (T/\text{K} - 283.15)^2 \quad (29)$$

$$B/\text{MPa} = 496.8 - 1.764(T/\text{K}) + 1.789 \times 10^{-3} (T/\text{K})^2 \quad (30)$$

The experimental specific volume values at  $p_0 = 0.1$  MPa are described with an AARD of 0.022% and those at higher pressures with an AARD of 0.035%. López *et al.* [45] also reported the isobaric thermal expansivity; compressibilities, both isothermal and isentropic; high pressure isobaric heat capacities; and the speed of sound at the same ranges of temperature and pressure.

Harris [30] measured experimental viscosities for DiPEiC<sub>9</sub> at temperatures between 293 and 363 K at pressures up to 203 MPa and viscosities between 34 and 2269 mPa s. Bair and Yamaguchi [46] measured low-shear viscosities at temperatures of 323 K, 343 K, and 363 K at pressures from 62 to 700 MPa, obtaining values between 1.257 and 8660 Pa s. These authors indicated that the agreement of their viscosities with those of Harris [18] is excellent, the deviations being less than 6% where there is overlap, except at 363 K, where the deviations are 8%.

Harris [30] correlated his values using two modified VFT equations and a modified Barlow-Lamb equation. The three correlations have similar qualities of fit. In the case of eq. (23), the fitted parameter values are  $a = -2.4221$ ,  $b = 3.134 \cdot 10^{-3} \text{ MPa}^{-1}$ ,  $c = -2.160 \cdot 10^{-5} \text{ MPa}^{-2}$ ,  $d = 1005.3 \text{ K}$ ,  $e = 3.620 \text{ MPa}^{-1} \cdot \text{K}$ ,  $f = -3.560 \cdot 10^{-3} \text{ MPa}^{-2} \text{ K}$ ,  $g = 1.498 \cdot 10^{-5} \text{ MPa}^{-3} \text{ K}$ , and  $T_0 = 193.31 \text{ K}$ . This correlation covers a temperature range from 293.15 to 363.15 K at pressures between 0.1 MPa and 203 MPa and viscosities between 34 and 2269 mPa s. The relative standard deviation is 1.3%. Deviation plots for this correlation and for the density correlations (eqs. 29, 30) can be found in [30, 45].

Using equations (17–19), Bair and Yamaguchi [46] correlated their viscosity values together with the elevated pressure values of Harris [30] and all his ambient pressure data. Hence, this correlation is valid from 293.15 to 363.15 K at high pressures up to 700 MPa. The values of the parameters are reported in Table 4.

Bair and Yamaguchi [46] have characterized the shear dependence of the viscosity of DiPEiC<sub>9</sub> at pressures up to 700 MPa and temperatures from 293.15 K to 363.15 K and shear stress up to 18 MPa. The flow curves

**Table 4:** Parameter values equations (18–20) for DiPEiC<sub>9</sub> [46] and relative standard deviation *s*.

$\eta_g/\text{Pa s}$	$T_{g0}/\text{K}$	$A_1/\text{K}$	$A_2/\text{GPa}^{-1}$	$b_1/\text{GPa}^{-1}$	$b_2$	$C_1$	$C_2/\text{K}$	$s$
$10^{12}$	222.01	164.6	0.9508	10.202	-0.3720	15.866	25.49	3.7 %

indicate an unusually high Newtonian stress limit (around a shear stress of 6 MPa at 294.15 K and 250 MPa). These authors also performed oscillatory shear measurements of DiPEiC<sub>9</sub> at atmospheric pressure and temperatures of 298.15 K, 313.15 K, and 333.15 K, in the frequency range of 5 MHz to 205 MHz. Oscillatory shear measurements confirm Newtonian response up to a shear stress of at least 8 MPa. According to the authors, the rotational relaxation of a DiPEiC<sub>9</sub> molecule is probably less retarded by friction with close neighbors than for squalane, as the rotations of the DiPEiC<sub>9</sub> molecules do not result in a substantial change in the aspect ratio presented to neighboring molecules, while for squalane this change is important.

## 6 Conclusions

During this project we have defined two International Standards for viscosity at temperatures up to 473 K and pressures below 200 MPa: squalane and tris(2-ethylhexyl) trimellitate (TOTM), which have viscosities of 5 mPa s and 10 mPa s, respectively, at  $T=473.15$  K and  $p=200$  MPa and satisfy all the other criteria to be standards. In addition, we have performed a round robin experimental study and correlations of several thermo-physical properties of Krytox GPL 102 over broad ranges of temperatures and pressures. Krytox GPL 102 has a viscosity of 25 mPa s at  $T=473.15$  K and  $p=200$  MPa and satisfies all the requirements to be an International Viscosity Standard, close to the industrial criteria of nominal viscosity of 20 mPa s at a temperature of 473 K and pressure of 200 MPa, except that it is not a pure substance. This last fact prevents it from being a standard because lot-to-lot variation can occur. For example, as indicated earlier, Fortin *et al.* [27] found viscosity deviations between 7 % and 15 % for two specified lots at atmospheric pressure and temperatures from 263.15 K to 373.15 K. Furthermore, for more viscous liquids, such as heavier oils and lubricants, experimental and theoretical studies were performed for dipentaerythritol hexa(3,5,5-trimethylhexanoate), for which  $\eta(473.15$  K, 200 MPa) is around 80 mPa s. In this case, it satisfies all the requirements to be an International Standard, except that it is not commercially available. Nevertheless, a lubricant company has recently provided several litres to a number of laboratories for scientific purposes. This means that if this compound is identified as Standard a company could be interested in producing and selling this single compound with high chemical purity and at a reasonable cost. In the future, other complex esters could likely meet all the requirements.

## Membership of sponsoring bodies

This article summarises the measurements and procedures developed for IUPAC, Funder Id: 10.13039/100006987, Project 2012-051-1-100 [International standard for viscosity at temperatures up to 473 K and pressures below 200 MPa], chaired by Josefa Fernandez (Universidade de Santiago de Compostela, Spain). Members of the project task group were Marc J. Assael (Aristotle University, Thessaloniki, Greece), Robert M. Enick (University of Pittsburgh, USA) and J. P. Martin Trusler (Imperial College London, UK).

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