High Pressure Viscosity Behaviour of tris(2-ethylhexyl) trimellitate up to 150 MPa

José M. Liñeira del Río, María J.G. Guimarey, María J.P. Comuñas*, Josefa Fernández

Laboratorio de Propiedades Termofísicas, Grupo NaFoMat, Departamento de Física Aplicada, Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Spain

* Corresponding author: M.J.P. Comuñas

E-mail address: mariajp.comunas@usc.es

ABSTRACT

This article presents a study on the viscous behavior at high pressure of a synthetic oil, tris(2-ethylhexyl) trimellitate (TOTM). This fluid is being recommended as potential industrial reference material for high viscosity-high pressure measurements. Here we report new experimental viscosity values for TOTM at temperatures from 278.15 to 373.15K and at pressures to 150 MPa with a maximum viscosity of 2570 mPa.s. The measurements have been performed using a high pressure falling-body apparatus and a Couette rotational viscometer. The experimental values obtained in this work are included in the database of a multinational project used recently to develop a reference correlation for TOTM (Wakeham et al, J. Chem. Eng, Data, 62, 2884, 2017). The universal viscosity-pressure coefficient of this fluid has been evaluated and compared with other oils, finding that it is close to the literature values of mineral oils. Moreover, we perform an analysis of the dependency of viscosity on pressure and temperature based on the density scaling concept.

Keywords: Tris(2-ethylhexyl) trimellitate, Viscosity, High Pressure.

1. Introduction

One of the most serious limitations for experimentally determining the viscosity at different pressures for viscous samples, for most of the currently used techniques, is the necessity of a calibration with appropriate reference fluid. This calibration should be usually performed over the measuring temperature and pressure interval for different viscosity ranges [1]. For several fluids of economic significance in industrial and commercial activities, as crude oils or lubricants, usually, it is necessary to know viscosity in broad ranges of temperatures and pressures, but in these conditions, viscosity changes over several orders of magnitude. Consequently, a single reference fluid could be not enough to cover this wide range of viscosity. Therefore, a large range of standard liquids should be available for viscosity calibration [2]. For this reason, in the framework of a IUPAC project (2012–051–1–100) several members of International Association for Transport Properties (IATP) aim to select reference standard materials for high pressure and high temperature, specifically, with viscosity around 20 m Pa s at 473 K and 200 MPa [3; 4]. One of the fluids that has been recently proposed as industrial reference material for high viscosity is tris(2-ethylhexyl) trimellitate (TOTM) [5]. This fluid is liquid at atmospheric pressure and ambient temperature, which is an essential requirement for viscosity standards. TOTM is a triester is an important plasticizer in the polymer industry [3; 5-7]. Besides, trimellitate esters present a number of characteristics that make them suitable for wide applications as a lubricant, such as to have a low vapour pressure, high viscosities and to be liquid over a large temperature range [8].

Several works have been published on viscosity of TOTM. Thus, Lorenzi et al. [9] have measured viscosity of this fluid from 298.15 K to 368.46 K at 0.1 MPa by using a Ubbelohde capillary viscometer. Diogo et al [5; 7] have reported viscosity at high pressure of two different lots of TOTM (MKBH8084V and MKBQ0304V) in the range of temperatures from (303 to 373) K up to 100 MPa. These authors have used both, a capillary Ubbelohde and a vibrating wire viscometer. Bair et al. [10] experimentally determined the viscosity behavior at high pressures of TOTM (lot MKBQ0304V) in different conditions, using two falling body viscometers: one from 313.15 to 423.15 K up to 350 MPa named in this work as low medium pressure viscometer (LMP) and other one from 313.15 to 373 K and from 100 MPa to 1000 MPa designated by medium high pressure viscometer (MHP). Baled et al. [11] measured the viscosity at high pressure (lot number: MKBT5164V) from 314 to 523 K, in a pressure range from 3.5 MPa to 270 MPa using a rolling ball viscometer. Assael and Tsolakidou [12] determined the rheological behaviour at atmospheric pressure from 293.15 to 353.15 K ~~at 0.1 MPa~~ finding that TOTM has a Newtonian behaviour at shear stresses from 25 to 107 Pa and at shear rates from 100 to 501 s^{-1}. Recently, Avelino et al. [13] have also studied the rheological behaviour of TOTM at 0.1 MPa but for shear stresses to 750 Pa and shear rates up to 4000 s^{-1}. These authors [13] have observed that this fluid has a Newtonian behaviour at shear rates lower than 600 s^{-1}, for higher values TOMT is shear thinning. The shear dependence of the viscosity of TOTM at pressures from 600 MPa to 700 MPa have also been determined by Bair [3] using shear stresses up to 15 MPa. Bair has found that TOTM can be considered as Newtonian for stresses lower than 5 MPa, for higher values the viscosity decreases with increasing shear stress. Non-Newtonian effects are not expected in normal high-pressure viscometer measurements [4]. Thus, the rheological behavior of TOTM is considered entirely compatible with its use as an industrial calibrating fluid for viscosity [13]. In the present work, we report dynamic viscosity data of TOTM from 278.15 K to 373.15 K at high pressures (to 150 MPa).

2. Experimental

2.1. Materials

Three Cannon certified viscosity oils, N75, N100 and S600, were used as calibration fluids whereas squalane (CAS 111-01-3) was used as verification fluid. The squalane sample (Sigma–Aldrich) has a specified mole-fraction purity of 0.99 experimentally determined by gas chromatographic analysis. The sample of tris(2-ethylhexyl) trimellitate or 1,2,4-benzenetricarbixylic acid tris(2-ethylhexyl) ester (CAS 3319-31-1) studied in this work (Figure 1) was supplied by Sigma-Aldrich. The lot number of the TOTM sample is MKBT5164V, it has a mole fraction purity higher than 0.99 and a molecular weight of 546.789 g/mol. The purities and other specifications of chemicals are listed in Table 1.

2.2. Measurement techniques

Dynamic viscosities and densities at atmospheric pressure were measured by using a rotational automated viscometer-densimeter Anton Paar Stabinger SVM3000. This apparatus can operate from 278.15 to 373.15 K, reporting directly the corrected density values (i.e. effect of the sample viscosity on the density) [14]. Experimental expanded uncertainty of 1% and 5 10^{-4} g cm^{-3} have been estimated for dynamic viscosity and density, respectively [1; 14].

Viscosities at high pressure were measured using a falling body viscometer, VisLPT1, which can operate at pressures up to 150 MPa. This device has been further described in previous articles [15-17]. Four Pt100 temperature probes were installed around the inner tube instead of the thermocouple originally employed. The expanded uncertainty of these thermometers was ± 0.1 K. The liquid is compressed by means of a manual pressure generator HiP (model 50-5.75-30) and the pressure is measured by a transducer (HBM P3MB) and a numeric indicator (HBM Scout 55) with an expanded uncertainty of ± 0.2 MPa. The hemispherical sinker employed in this work is the same as that used in the previous works [15-17]. It is made of magnetic steel and it has a diameter of 6.10 mm and a length of 20 mm.

The measuring principle of a falling body viscometer consists on the relationship between the fluid viscosity (η) and the time (Δt) that a solid takes to fall inside the inner tube through the fluid (once the solid has reached the terminal velocity working in a laminar flow) [18]. The working equation employed in this work is:

$$\eta(p,T) = \frac{t(1-\rho/\rho_s)}{A\left[1+2\alpha_{vt}(T-T_{ref})\right]\left[1-2\beta_{vt}(p-p_{ref})/3\right]} \tag{1}$$

where t is the falling time, ρ and ρ_s are the densities for the fluid and for the sinker, respectively, at the temperature T and pressure p. A is a calibration constant, and α_{vt} and β_{vt}, are the coefficients of expansion and compressibility of the viscometer tube (INCONEL 718) at reference conditions: T_{ref} = 298.15 K and p_{ref} = 0.1 MPa. This equation has the advantage that the parameter A is not dependent on either pressure or temperature; therefore, the calibration procedure can be performed at atmospheric pressure with certificated standard oils. This type of equation has been successful used for similar viscometers to measure fluids with low and high viscosity [19-21].

Density of the sinker for each p and T condition is calculated with the following equation [19]:

$$\rho_s(p,T) = \frac{\rho_s(p_{ref},T_{ref})}{\left[1+3\alpha_s(T-T_{ref})\right]\left[1-\beta_s(p-p_{ref})\right]}, \tag{2}$$

where $\rho_s(p_{ref},T_{ref})$ = 7.695 g cm^{-3}, whereas α_s and β_s are the coefficients of expansion and compressibility of the sinker (X4CrNiMo16-5-1) at reference conditions T_{ref} = 298.15 K and p_{ref} = 0.1 MPa. Values of the expansion coefficients are α_s = 10.8 10^{-6} K^{-1} and α_{vt} = 12.8 10^{-6} K^{-1}, respectively, whereas for compressibility, these are β_s = 5 10^{-6} MPa^{-1} and β_{vt} = 4.8 10^{-6} MPa^{-1}. Calibration constant, A, for equation (2) is estimated from viscosity reference fluids. We have performed the calibration procedure at atmospheric pressure from 293.15 to 353.15 K with the three Cannon certified viscosity oils. These fluids cover the viscosity range from 14.5 m Pa s up to 1482 m Pa s. The value of the calibration constant A is 1.206 ± 0.003 Pa^{-1}. Taking into account uncertainties of temperature, pressure, falling times, calibration constant and densities of both sinker and fluid, the uncertainty of the device is estimated to be 3.5% with a coverage factor k=2. In order to verify the calibration procedure viscosity of squalane has been measured (Table 2) and compared with two different correlations proposed by Mylona et al. [22] finding AADs% of 1.4 % and 1.6 % and maximum deviations of 3.9% and 4.3%. These deviations confirm the reliability of the equipment.

3. Results and discussion

Experimental density and viscosity values at atmospheric pressure obtained with Anton Paar Stabinger SVM3000 apparatus are reported in Table 3. Density values at atmospheric pressure agree within an AAD of 0.08% with previous data reported by Bazile et al. [23], an AAD of 0.10% with Diogo et al [6], and AAD of 0.06% with Lorenzi et al. [9], and an AAD of 0.11% with Avelino et al. [13]. Finally, the average absolute deviation with the reference density correlation proposed by Wakeham et al. [3] is 0.06%. The viscosity at 0.1 MPa ranges from 9 to 976 m Pa s over the temperature interval 278.15 to 373.15 K. The viscosity index of TOTM has also been determined with SVM3000 apparatus obtaining a value of 89. Falling time measurements of TOTM were carried out at six different isotherms (303.15, 313.15, 323.15, 333.15, 343.15 and 353.15) K and at pressures up to 150 MPa. In equation 1 density data at each temperature and pressure are necessary to obtain dynamic viscosities. These values have been taken from the reference correlation for density recently proposed by Wakeham et al. [3] which covers the temperature range (293 to 523) K and pressures to 250 MPa. We must point out that our density values at 0.1 MPa and from 303.15 to 373.15 K (Table 3) agree with this reference correlation with an absolute average deviation of 0.06%. The viscosities at high pressures for tris(2-ethylhexyl) trimellitate are presented in Table 4 and range from 18 m Pa s at 353.15 K and 10 MPa to 2570 m Pa s at 303.15 K and 150 MPa. Viscosity values obtained with both devices (the high pressure falling-body apparatus and the rotational viscometer) are fitted together using four different equations as a function of pressure and temperature. These fitting equations have the following expressions:

$$\eta(p,T) = A\exp\left(\frac{B}{T-C}\right)\left(\frac{p+E(T)}{p_{ref}+E(T)}\right)^{D} \tag{3}$$

where $E(T)$ is a second-degree polynomial $E(T) = E_0 + E_1T + E_2T^2$, A, B and C are obtained fitting viscosity data at the reference pressure (0.1 MPa) as a function of temperature and D as well as E_0, E_1 and E_2 by adjustment of the experimental viscosities at high pressures. Equation (3), proposed by Comuñas et al. [24], is a modified Vogel-Fulcher-Tammann equation as well as the following two equations, which were proposed by Harris et al. [25]:

$$\eta(p,T) = \exp\left(a + bp + \frac{c + dp + ep^2}{T - T_0}\right) \tag{4}$$

$$\eta(p,T) = \exp\left(a + bp + c\frac{T_0(p)}{T - T_0(p)}\right) \tag{5}$$

where $T_0(p) = d + e\cdot p + f\cdot p^2$.

The values of the parameters of equations (3-5) are gathered in Table 5. These equations lead to good correlations of the experimental values in all cases with AADs lower than 2%. The correlated curves using equation (4) together all the experimental viscosities of TOTM measured in this work are plotted in Figure 2. The viscosity values obtained from equation (3) at 0.1 MPa agree with those previously reported by Lorenzi et al. [9] within a maximum deviation, MaxD%, of 2% (at 318 K) and an average deviation, AAD%, of 1.3% over the entire temperature range. MaxD% and AAD% values are 0.6% (at 328 K) and 0.3%, respectively, with the experimental viscosities provided by Diogo et al [5]. High-pressure viscosity comparisons have also been carried out with the data obtained by other authors using different measuring equipment. We specify also the lot number used for the TOTM sample. We have compared the values that are inside the limits of our temperature and pressure ranges, that is, we have avoided extrapolation. The first comparison has been made with the values obtained by Baled et al. [11] using a rolling ball viscometer with an expanded uncertainty of 3% (k=2), since these authors use the same lot number (MKBT5164V) than that used in the present work. Baled et al. [11] use two different expressions (equation 7 and 9 of reference [11]) to correlate their viscosity data. For both equations (7 and 9 of reference [11]), average deviations around 3% were found with our experimental. viscosities (Table 4). With equation (7), we obtain a maximum deviation of 5.3% at 75 MPa and 313 K, while for equation (9) the maximum deviation (6.6%) appears at 100 MPa and 313 K. In figure 3, we present the relative deviations as a function of the temperature between the experimental viscosity values reported in Table 4 and those obtained from equation (7) and equation (9) of reference [11]. The expanded uncertainty of the relative deviations obtained with both equations is around 5%. Taking into account this uncertainty we have concluded that 90% of the points compared with Baled et al. [11] are within this expanded uncertainty.

As regards to the comparison with literature viscosity measurements of other lots of TOTM, Diogo et al. [5; 7] measured the viscosity at high pressure of two TOTM samples (lot numbers MKBH8084V and MKBQ0304V) with a vibrating wire viscometer with expanded uncertainties (k=2) from 2% to 3%. With the first lot [5], a relative average deviation of 3.5% and a maximum deviation of 8.4% (at 65.49 MPa and 328.16 K) are obtained from equation (3) of the present work and their experimental values. MaxD% and AAD% are 4.9% and 8.8% (at 80.22 MPa and 313.15 K), respectively, for the second lot [7]. We have compared the values obtained with equation (3) with the experimental viscosities reported by Bair [10] for the sample with lot number MKNQ0304V using both, the LMP and MHP viscometers, with nominal uncertainties of 3%. With the viscosities obtained from LMP viscometer, we obtain an average deviation of 6.1% and a maximum deviation around 9.5% (at 313 K and 100 MPa). With the MHP, we obtain absolute average deviations of 0.1% (for 313.15 K and 100 MPa) and 2.7% (for 313.15 K and 150 MPa). In Figure 3 the relative deviations obtained between the correlated values given by equation 3 and the experimental data of Diogo et al. [5; 7] and Bair [10] are also included. We must point out that the average deviations obtained with all these authors [5; 7; 10; 11] are within the combined expanded uncertainties. All the lots used in the last articles [5; 7; 10; 11] were provided by Sigma-Aldrich with a certificate of analysis stating a mole fraction purity higher than 0.99. Previous comparisons among viscosity and other properties of the different lots were reported by Wakeham et al. [3]. Finally, we must mention that the viscosity data reported in Tables 3 and 4 present an average relative deviation of 3.4% with the reference correlation recently reported [3] for TOTM. A deviation plot including all above indicated literature viscosity data [5; 7; 10; 11], as well as the η reported in this work, were already published by Wakeham et al. [3].

To study the pressure and temperature effect on viscosity, the pressure-viscosity (α) and temperature-viscosity (β) coefficients are analyzed. These two parameters are important to characterize lubricants and can be calculated by differentiation as follows:

$$\alpha(p) = \frac{1}{\eta\,(p,T)}\left(\frac{\partial\eta\,(p,T)}{\partial p}\right)_T \tag{6}$$

$$\beta(T) = -\frac{1}{\eta\,(p,T)}\left(\frac{\partial\eta\,(p,T)}{\partial T}\right)_p \tag{7}$$

Using equation (3) both coefficients can be expressed as:

$$\alpha(p) = \frac{D}{E(T)+p} \tag{8}$$

$$\beta(T) = \frac{B}{(T-C)^2} + D\frac{E'(T)\cdot(p-0.1)}{(0.1-E(T))(p+E(T))} \tag{9}$$

where $E'(T) = E_1 + 2E_2T$ is the derivative of *E*(T).

The values of the pressure-viscosity and temperature-viscosity coefficients obtained for TOTM are reported in Table 6. In Figure 4, we can observe that the decrease of α with the temperature is very similar for all the isobars (around 30%). The temperature-viscosity coefficient is shown in Figure 5 as a function of the pressure. This coefficient (β) increases with the pressure, around 21% for all the temperatures. TOTM β values are strongly bigger than those obtained for other mineral and vegetable lubricant as well as glycols and esters [26-28]. The high TOTM β values are in agreement with the low viscosity values, because both parameters reflect the variation of the viscosity with the pressure but in opposite ways. According the American Gear Manufacturers Association working in an elastohydrodynamic regime of lubrication, keeping geometry, elastic properties, speed and load fixed, the central film thickness is a function of the pressure-viscosity coefficient (α) and the absolute viscosity (η_0) through the following expression [29]:

$$h_{cent}/(\mu m) \propto (\eta_0\,/\,mPa\cdot s)^{0.69}(\alpha_{film}/\,GPa^{-1})^{0.56} \tag{10}$$

According to Bair et al. [30] the universal pressure-viscosity coefficient (α_{film}) can be estimated with the expression:

$$\alpha = \alpha_{film} = \frac{1-\exp(-3)}{p_{iv}(3/\alpha*)}, \tag{11}$$

where p_{iv} the isoviscous pressure given by:

$$p_{iv} = \int_0^p \frac{\eta(p'=0)dp'}{\eta(p')} \tag{12}$$

and α^* is the reciprocal asymptotic isoviscous pressure coefficient:

$$\alpha* = \frac{1}{p_{iv}(\infty)} = \left[\int_0^\infty \frac{\eta(p=0)dp}{\eta(p)}\right]^{-1} \tag{13}$$

In lubricating oils in order to avoid wear, high values of film thickness are required, although on the other hand, low values are required to save friction energy, reduce subsurface stress as well as pressure peaks. In Table 7, it can be seen the universal pressure-viscosity coefficient (α_{film}), the reciprocal asymptotic isoviscous pressure ($\alpha*$) and the product $\eta_0^{0.69}\alpha_{film}^{0.56}$ for TOTM. The obtained values of the reciprocal asymptotic isoviscous pressure coefficient, $\alpha*$, are slightly lower than those of α_{film} for the studied temperature range. Usually, use of $\alpha*$ tends to underestimate the film thickness [27; 31]. We have compared the values estimated for $\alpha*$ with those previously reported by Bair [10] for another lot (MKNQ0304V), obtaining relative deviations between both data series of 4.2% and 1.3% at 313.15 K and at 343.15 K, respectively. For α_{film}, AADs% are 5.4% (313.15K) and 2.4% (343.15K). In Figure 6, the values of the universal pressure-viscosity coefficient (α_{film}) of several viscous fluids are compared. We can see that the TOTM α_{film} value is quite similar to those of mineral oils and much lower than that of another reference fluid (Krytox GPL 102 [10]). This is due to big differences between the

the molecules of the last oil ($F[CF(CF_3)CF_2O]_nCF_2CF_3$ with an average value for n of 9.528) with respect to those of the other base fluids (esters, glycols and mineral oils). In Figure 7, we can observe the temperature dependence of the product $\eta_0^{0.69}\alpha_{film}^{0.56}$ for TOTM, its value is six times bigger at 303.15 K than at 353.15 K. This means that the film thickness created by the TOTM decrease very strongly when the temperature rises. This fact is not only due to the decrease of the α_{film} values with the temperature but also to the big decrease of the viscosity of this compound with the temperature (low viscosity index and high β values).

Many authors have reported [32-34] that several dynamic properties can be expressed as functions of the temperature, *T*, and volume, *V*, through a scaling relation as follows:

$$x(T,V) = \psi\left(TV^{\gamma}\right) \tag{14}$$

where *x* is a dynamic property (dielectric relaxation time, τ, viscosity, η, self-diffusion coefficient, *D*, or electrical conductivity, κ). The constant γ is an empirically determined parameter (scaling parameter) which reflects the repulsive intermolecular force, although for complex molecules or ions it can also include contributions from internal molecular modes, such as vibrations and torsions, and be affected by the attractive intermolecular forces [35]. Pensado et al. [35] and López et al. [36] have used the following expression to determine γ values from the dynamic viscosity of several molecular and ionic liquids:

$$\eta(T,\rho) = \eta_0 \exp\left[\left(\frac{\rho^{\gamma} A}{T}\right)^{\phi}\right] \tag{15}$$

where *T* is the temperature, ρ is the density, and η_0, *A*, γ and ϕ may be used as fit parameters. Fragiadakis and Roland [37] and Galliero et al. [38] have proposed writing the transport properties in reduced forms when superposition curves are performed. In reduced form, the comparison among molecular simulation results and experimental transport data becomes more straightforward. The difference between scaling using reduced rather than unreduced units is negligible in the supercooled regime; however, at higher temperature the difference can be substantial, accounting for the purported breakdown of the scaling and giving rise to different values of the scaling exponent. Only the γ obtained using reduced quantities can be sensibly related to the intermolecular potential. The use of reduced quantities for viscosity, electrical conductivity and self-diffusion coefficients leads to values of the scaling parameter that are closer than when unreduced quantities are considered [37; 39]. The reduced form for the viscosity is as follows:

$$\eta^* = v^{2/3}\left(mk_B T\right)^{-1/2}\eta \qquad (16)$$

where m is the molecular mass and v the liquid volume per molecule (v=V/N, being N the total number of molecules in a liquid volume V). Subsequently, equation 15 can be rewritten as:

$$v^{2/3}\left(mk_B T\right)^{-1/2}\eta(T,\rho) = \eta_0^* \exp\left[\left(\frac{\rho^{\gamma^*}A^*}{T}\right)^{\phi^*}\right] \qquad (17)$$

Equation 17 has been used previously [36; 39] to determine the reduced scaling thermodynamic parameter for ionic liquids, alkanes, esters, alcohols, polyethers, dialkyl carbonates among other fluids. In this work, the scaling exponent γ^* was determined for TOTM by using viscosity data reported in Tables 3 and 4 as well as the density data obtained from the reference correlation recently proposed by Wakeham et al. [3]. Equation 17 represents the reduced dynamic viscosities of TOTM with an average absolute deviation of 1.3%. Relative deviations between the η^* values obtained from Tables 3 and 4 and those achieved with equation 17 are plotted in Figure 8a. There is no systematic trend with pressure or temperature. We obtain the following values for the parameters, η_0^*= 7.3374 m Pa s, A^* = 833.90 K $g^{-\gamma}$ $cm^{3\gamma}$, γ^*= 3.3 and ϕ^*= 1.85. Bair [10] has also estimated the scaling parameter for TOTM from non-reduced viscosity values. Comparing both scaling exponents we found that the reduced scaling exponent, γ^*, obtained in this work is slightly lower than the γ due to Bair ($\gamma = 3.66$). This fact is in agreement with the results of López et al. [36] for other fluids. In Figure 8b, we have plotted the reduced viscosity for TOTM as function of $1000\rho^{\gamma^*} T^{-1}$. The γ^* value of TOTM is also quite similar to those previously obtained [21] using non reduced viscosity for other types of ester lubricants: bis(2-ethylhexyl) phthalate DEHP ($\gamma = 3.65$), diisodecyl phthalate DIDP ($\gamma = 3.96$) and 2-ethylhexyl benzoate EHB ($\gamma = 3.69$).

4. Conclusions

Detailed experimental investigation on effects of pressure and temperature on viscous behavior of TOTM was carried out. These experimental viscosity values were already used to develop a reference correlation for this fluid in the background of an IUPAC international project (2012–051–1–100) proposed by the International Association for Transport Properties. The viscosity of this fluid increases from 18 to 2570 m Pa s over the pressure and temperature intervals analyzed. The reported data agree within the combined experimental uncertainties with previous viscosity data reported for this fluid with samples of same or different lot numbers. The lubrication ability of TOTM was also analyzed, finding that its universal viscosity-pressure coefficient is similar to those of mineral oils and much lower than that of another reference fluid (Krytox GPL 102). The obtained reduced scaling exponent is slightly lower that the values previously determined from no-reduced viscosity and quite similar to those of other types of ester lubricants.

Acknowledgements

This work was supported by both the Spanish Ministry of Economy, Industry and Competitiveness and the European Regional Development Fund through the ENE2014-55489-C2-1-R and ENE2017-86425-C2-2-R projects. Authors acknowledge the financial support by the Xunta de Galicia through GRC ED431C 2016/001 and ED431E 2018/08 grants. The measurements of TOTM were carried out under the auspices of the International Union of Pure and Applied Chemistry (IUPAC) within the framework of the Project No. 2012–051–1–100.

5. References

[1] X. Paredes, O. Fandiño, M.J.P. Comuñas, A.S. Pensado, J. Fernández, Study of the effects of pressure on the viscosity and density of diisodecyl phthalate, J. Chem. Thermodyn. 41 (2009) 1007-1015. https://doi.org/10.1016/j.jct.2009.04.002

[2] F.J.P. Caetano, J.M.N.A. Fareleira, A.P. Fröba, K.R. Harris, A. Leipertz, C.M.B.P. Oliveira, J.P.M. Trusler, W.A. Wakeham, An Industrial Reference Fluid for Moderately High Viscosity, J. Chem. Eng. Data 53 (2008) 2003-2011. 10.1021/je800059n

[3] W.A. Wakeham, M.J. Assael, H.M.N.T. Avelino, S. Bair, H.O. Baled, B.A. Bamgbade, J.-P. Bazile, F.J.P. Caetano, M.J.P. Comuñas, J.-L. Daridon, J.C.F. Diogo, R.M. Enick, J.M.N.A. Fareleira, J. Fernández, M.C. Oliveira, T.V.M. Santos, C.M. Tsolakidou, In Pursuit of a High-Temperature, High-Pressure, High-Viscosity Standard: The Case of Tris(2-ethylhexyl) Trimellitate, J. Chem. Eng. Data 62 (2017) 2884-2895. 10.1021/acs.jced.7b00170

[4] J. Fernández, M.J. Assael, R.M. Enick, J.P.M. Trusler, International Standard for viscosity at temperatures up to 473 K and pressures below 200 MPa (IUPAC Technical Report), Pure Appl. Chem. 91 (2018) 161-172.

[5] J.C.F. Diogo, H.M.N.T. Avelino, F.J.P. Caetano, J.M.N.A. Fareleira, Tris(2-ethylhexyl) trimellitate (TOTM) a potential reference fluid for high viscosity. Part I: Viscosity measurements at temperatures from (303 to 373)K and pressures up to 65MPa, using a novel vibrating-wire instrument, Fluid Phase Equilib. 384 (2014) 50-59. https://doi.org/10.1016/j.fluid.2014.10.002

[6] J.C.F. Diogo, H.M.N.T. Avelino, F.J.P. Caetano, J.M.N.A. Fareleira, Tris(2-Ethylhexyl) trimellitate (TOTM) a potential reference fluid for high viscosity. Part II: Density measurements at temperatures from (293 to 373)K and pressures up to 68MPa, Fluid Phase Equilib. 384 (2014) 36-42. https://doi.org/10.1016/j.fluid.2014.10.003

[7] J.C.F. Diogo, H.M.N.T. Avelino, F.J.P. Caetano, J.M.N.A. Fareleira, W.A. Wakeham, Tris(2-ethylhexyl) trimellitate (TOTM) as a potential industrial reference fluid for viscosity at high temperatures and high pressures: New viscosity, density and surface tension measurements, Fluid Phase Equilib. 418 (2016) 192-197. https://doi.org/10.1016/j.fluid.2016.01.012

[8] L.R. Rudnick, S.Z. Erhan, Synthetic, Mineral Oils and Bio-based Lubricants, 2013.

[9] L. De Lorenzi, M. Fermeglia, G. Torriano, Density, Kinematic Viscosity, and Refractive Index for Bis(2-ethylhexyl) Adipate, Tris(2-ethylhexyl) Trimellitate, and Diisononyl Phthalate, J. Chem. Eng. Data 43 (1998) 183-186. 10.1021/je970200z

[10] S. Bair, The temperature and pressure dependence of viscosity and volume for two reference liquids, Lub. Sci. 28 (2016) 81-95. doi:10.1002/ls.1302

[11] H.O. Baled, D. Tapriyal, I.K. Gamwo, B.A. Bamgbade, M.A. McHugh, R.M. Enick, Viscosity Measurements of Two Potential Deepwater Viscosity Standard Reference Fluids at High Temperature and High Pressure, J. Chem. Eng. Data 61 (2016) 2712-2719. 10.1021/acs.jced.6b00128

[12] M.J. Assael, M. Ch.Tsolakidou, Rheological behaviour of TOTM from 20 to 80ºC a 0.1 MPa, Personal communication (2018)

[13] H. Avelino, F.J.P. Caetano, J.C.F. Diogo, J.M.N.A. Fareleira, M.F.V. Pereira, F.J.V. Santos, T.V.M. Santos, W.A. Wakeham, Density and Rheology of Tris(2-ethylhexyl) Trimellitate (TOTM), J. Chem. Eng. Data 63 (2018) 459-462. 10.1021/acs.jced.7b00939

[14] M. Dakkach, F.M. Gaciño, S.K. Mylona, M.J.P. Comuñas, M.J. Assael, J. Fernández, High pressure densities of two nanostructured liquids based on the bis(trifluoromethylsulfonyl)imide anion from (278 to 398) K and up to 120 MPa, J. Chem. Thermodyn. 118 (2018) 67-76. https://doi.org/10.1016/j.jct.2017.10.012

[15] M.J.P. Comuñas, X. Paredes, F.M. Gaciño, J. Fernández, J.P. Bazile, C. Boned, J.L. Daridon, G. Galliero, J. Pauly, K.R. Harris, M.J. Assael, S.K. Mylona, Reference Correlation of the Viscosity of Squalane from 273 to 373 K at 0.1 MPa, J. Phys. Chem. Ref. Data 42 (2013) 033101. https://doi.org/10.1063/1.4812573

[16] M.J.P. Comuñas, X. Paredes, F.M. Gaciño, J. Fernández, J.-P. Bazile, C. Boned, J.-L. Daridon, G. Galliero, J. Pauly, K.R. Harris, Viscosity measurements for squalane at high pressures to 350MPa from T=(293.15 to 363.15)K, J. Chem Thermodyn. 69 (2014) 201-208. https://doi.org/10.1016/j.jct.2013.10.001

[17] F.M. Gaciño, X. Paredes, M.J.P. Comuñas, J. Fernández, Effect of the pressure on the viscosities of ionic liquids: Experimental values for 1-ethyl-3-methylimidazolium ethylsulfate and two bis(trifluoromethyl-sulfonyl)imide salts, J. Chem. Thermodyn. 54 (2012) 302-309. https://doi.org/10.1016/j.jct.2012.05.007

[18] J. Kestin, W.A. Wakeham, Transport properties of fluids: Thermal conductivity, viscosity and diffusion coefficient, Purdue Research Foundation, New York, 1988.

[19] J.H. Dymond, K.J. Young, J.D. Isdale, Transport Properties of Nonelectrolyte Liquid Mixtures. II. Viscosity Coefficients forn-Hexane + n-Hexadecane System at Temperatures from 25 to 100 °C at Pressures up to the Freezing Pressure or 500 MPa. , Int.J. Thermophys. 1 (1980) 345-373.

[20] R. Malhotra, W.E. Price, L.A. Woolf, A.J. Easteal, Thermodynamic and transport properties of 1, 2-dichloroethane, Int. J. Thermophys. 11 (1990) 835-861. 10.1007/BF00503578

[21] K.R. Harris, Temperature and Pressure Dependence of the Viscosities of 2-Ethylhexyl Benzoate, Bis(2-ethylhexyl) Phthalate, 2,6,10,15,19,23-Hexamethyltetracosane (Squalane), and Diisodecyl Phthalate, J. Chem. Eng. Data 54 (2009) 2729-2738. 10.1021/je900284z

[22] S.K. Mylona, M.J. Assael, M.J.P. Comuñas, X. Paredes, F.M. Gaciño, J. Fernández, J.P. Bazile, C. Boned, J.L. Daridon, G. Galliero, J. Pauly, K.R. Harris, Reference Correlations for the Density and Viscosity of Squalane from 273 to 473 K at Pressures to 200 MPa, J. Phys. Chem. Ref. Data 43 (2014) 013104. 10.1063/1.4863984

[23] J.-P. Bazile, D. Nasri, J.-L. Daridon, Speed of Sound, Density, and Derivative Properties of Tris(2-ethylhexyl) Trimellitate under High Pressure, J. Chem. Eng. Data 62 (2017) 1708-1715. 10.1021/acs.jced.7b00162

[24] M. Comuñas, A. Baylaucq, C. Boned, J. Fernández, High-pressure measurements of the viscosity and density of two polyethers and two dialkyl carbonates, Int. J. Thermophys. 22 (2001) 749-768.

[25] K.R. Harris, L.A. Woolf, M. Kanakubo, T. Rüther, Transport Properties of N-Butyl-N-methylpyrrolidinium Bis(trifluoromethylsulfonyl)amide, J. Chem. Eng. Data 56 (2011) 4672-4685. 10.1021/je2006049

[26] X. Paredes, M.J.P. Comuñas, A.S. Pensado, J.-P. Bazile, C. Boned, J. Fernández, High pressure viscosity characterization of four vegetable and mineral hydraulic oils, Ind. Crops Prod. 54 (2014) 281-290. https://doi.org/10.1016/j.indcrop.2014.01.030

[27] X. Paredes, O. Fandiño, A.S. Pensado, M.J.P. Comuñas, J. Fernández, Pressure–Viscosity Coefficients for Polyalkylene Glycol Oils and Other Ester or Ionic Lubricants, Trib. Letters 45 (2012) 89-100. 10.1007/s11249-011-9861-z

[28] X. Paredes, O. Fandiño, A.S. Pensado, M.J.P. Comuñas, J. Fernández, Experimental density and viscosity measurements of di(2ethylhexyl)sebacate at high pressure, The Journal of Chemical Thermodynamics 44 (2012) 38-43. https://doi.org/10.1016/j.jct.2011.07.005

[29] R. Errichello, Selecting oils with high pressure-viscosity coefficient - Increase bearing life by more than four times, Machinery Lubrication, 2004.

[30] S. Bair, Y. Liu, Q.J. Wang, The Pressure-Viscosity Coefficient for Newtonian EHL Film Thickness With General Piezoviscous Response, J. Trib. 128 (2006) 624-631. 10.1115/1.2197846

[31] A.S. Pensado, M.J.P. Comuñas, J. Fernández, The Pressure–Viscosity Coefficient of Several Ionic Liquids, Trib. Letters 31 (2008) 107-118. 10.1007/s11249-008-9343-0

[32] C.M. Roland, S. Bair, R. Casalini, Thermodynamic scaling of the viscosity of van der Waals, H-bonded, and ionic liquids, J. Chem. Phys. 125 (2006) 124508. 10.1063/1.2346679

[33] S. Bair, A. Laesecke, Normalized Ashurst-Hoover Scaling and a Comprehensive Viscosity Correlation for Compressed Liquids, J. Trib. 134 (2012) 021801-021801-021808. 10.1115/1.4005374

[34] R. Casalini, C.M. Roland, An equation for the description of volume and temperature dependences of the dynamics of supercooled liquids and polymer melts, J. Non-Cryst Solids 353 (2007) 3936-3939. https://doi.org/10.1016/j.jnoncrysol.2007.03.026

[35] A.S. Pensado, A.A.H. Pádua, M.J.P. Comuñas, J. Fernández, Relationship between Viscosity Coefficients and Volumetric Properties Using a Scaling Concept for Molecular and Ionic Liquids, J. Phys. Chem. B 112 (2008) 5563-5574. 10.1021/jp711752b

[36] E.R. López, A.S. Pensado, M.J.P. Comuñas, A.A.H. Pádua, J. Fernández, K.R. Harris, Density scaling of the transport properties of molecular and ionic liquids, J. Chem. Phys. 134 (2011) 144507. 10.1063/1.3575184

[37] D. Fragiadakis, C.M. Roland, On the density scaling of liquid dynamics, J. Chem. Phys. 134 (2011) 044504. 10.1063/1.3532545

[38] G. Galliero, C. Boned, J. Fernández, Scaling of the viscosity of the Lennard-Jones chain fluid model, argon, and some normal alkanes, J. Chem. Phys. 134 (2011) 064505. 10.1063/1.3553262

[39] F.M. Gaciño, X. Paredes, M.J.P. Comuñas, J. Fernández, Pressure dependence on the viscosities of 1-butyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide

and two tris(pentafluoroethyl)trifluorophosphate based ionic liquids: New measurements and modelling, J. Chem. Thermodyn. 62 (2013) 162-169. https://doi.org/10.1016/j.jct.2013.02.014

Table 1. Characteristics of the samples used in this work.

Chemical Name	*Source*	*Mole Fraction Purity*	*Analysis Method*
Tris(2-ethylhexyl)trimellitate (TOTM)	Sigma Aldrich	0.99	*a*
N75	Cannon	–	*b*
N100	Cannon	–	*b*
S600	Cannon	–	*b*
Water	–	–	*c*
Squalane (SQN)		0.99	*a*

[a] Gas chromatographic analysis determined by the supplier.

[b] Cannon™ Viscosity Standards: ASTM D 2162, ISO/IEC 17025, NIST certifications.

[c] Water sample purified using a Milli-Q plus system: resistivity of 18.2 MΩ cm and a total organic carbon smaller than 5 ng cm^{-3}.

Table 2

Experimental viscosity values, η/m Pa s, for squalane at different temperatures, T, and pressures, p determined with the falling body viscometer.

p/MPa	T/K			
	303.15	313.15	343.15	353.15
10	28.1	18.2	7.30	5.56
15	31.4	20.3	7.94	6.04
25	38.7	24.9	9.32	7.05
50	62.3	39.8	13.6	10.1
75	97.5	61.0	19.3	14.0
100	149.7	91.3	27.0	19.3
125	227.0	134.6	37.2	26.3
150	341.0	196.4	51.0	35.6

Expanded uncertainties (k=2) are $U(T)$ = ±0.1 K, $U(p)$ = ±0.2 MPa and $U_r(\eta)$ = 3.5%.

Table 3

Density and viscosity values obtained with the Anton Paar Stabinger SVM3000 for TOTM at atmospheric pressure (0.0992 MPa[a]).

T^{b}/ K	ρ^{c} / g cm^{-3}	η^{d} / m Pa s
278.15	0.9989	976.0
283.15	0.9956	636.6
288.15	0.9919	429.0
293.15	0.9884	296.9
298.15	0.9848	210.6
303.15	0.9812	152.9
308.15	0.9777	113.4
313.15	0.9742	85.76
318.15	0.9707	66.05
323.15	0.9671	51.74
328.15	0.9635	41.18
333.15	0.9600	33.26
338.15	0.9564	27.21
343.15	0.9528	22.53
348.15	0.9492	18.86
353.15	0.9456	15.96
358.15	0.9419	13.62
363.15	0.9383	11.74
368.15	0.9347	10.19
373.15	0.9312	8.92

[a] Expanded pressure uncertainty (k = 2, level of confidence = 0.95): 0.0005 MPa.

[b] Expanded temperature uncertainty (k = 2, level of confidence = 0.95): 0.02 K.

[c] Expanded density uncertainty (k =2, level of confidence = 0.95): 5 10^{-4} g cm^{-3}

[d] Relative expanded viscosity uncertainty (k = 2, level of confidence = 0.95): 1 % for all range of temperature.

Table 4

Experimental viscosity values, η/m Pa s, for tris(2-ethylhexyl) trimellitate (TOTM) at different temperatures, *T*, and pressures, *p* determined with the falling body viscometer.

p/MPa	*T*/K					
	303.15	313.15	323.15	333.15	343.15	353.15
10	188.3	100.8	62.2	41.1	26.3	18.1
15	211.6	112.6	68.9	45.3	28.9	19.7
25	263.2	139.0	83.8	54.3	34.4	23.3
50	434.0	225.9	131.8	82.3	51.6	34.6
75	692.9	353.9	200.2	121.3	75.4	50.0
100	1085	542.0	297.8	176.2	108.4	71.2
125	1678*	819.1	437.1	253.1	154.2	100.1
150	2570*	1227	636.2	360.5	217.8	139.9

Expanded uncertainties (*k*=2) are $U(T)$ = ±0.1 K, $U(p)$ = ±0.2 MPa and $U_r(\eta)$ = 3.5%.

* Expanded uncertainties (*k*=2) are $U(T)$ = ±0.1 K, $U(p)$ = ±0.2 MPa and $U_r(\eta)$ = 5.0%.

Table 5

Parameters of the correlation equations (3-5) for TOTM.

Parameters	*Equation (3)*
A/m Pa s	0.01740
B/K	1343.85
C/K	155.24
D	10.573
E_0/MPa	-1555.22
E_1/MPa	9.8527
$10^2\ E_2$/MPa	-1.0236
AAD/%	1.5
Bias/%	1.0
MaxD/%	7.3
	Equation (4)
A	-3.6516
$10^3\ b$/MPa^{-1}	1.5153
c/K	1235.56
d/K MPa^{-1}	2.7895
$10^5 e$/K MPa^{-2}	-220.871
T_0/K	160.87
AAD/%	1.1
Bias/%	-0.1
MaxD/%	4.5
	Equation (5)
A	-3.8637
$10^3\ b$/MPa^{-1}	7.3032
C	8.2271
d/K	157.530
$10^2\ e$/K MPa^{-1}	11.4127
$10^5\ f$/K MPa^{-2}	-17.087
AAD/%	1.2
Bias/%	0.3
MaxD/%	4.9

Table 6

Pressure-viscosity coefficients, $\alpha(p)$/GPa^{-1}, and temperature-viscosity coefficients, $\beta(T)$/K^{-1}, for the TOTM measured in this work.

p/MPa	T/K					
	303.15	313.15	323.15	333.15	343.15	353.15
			$\alpha(p)$/GPa^{-1}			
10	21.1	19.7	18.6	17.6	16.8	16.1
50	19.5	18.3	17.3	16.5	15.8	15.2
100	17.9	16.9	16.0	15.3	14.7	14.1
150	16.5	15.6	14.9	14.3	13.7	13.3
			$\beta(T)$/K^{-1}			
10	63.0	55.2	48.7	43.4	38.8	35.0
50	68.7	59.9	52.7	46.7	41.6	37.4
100	74.7	64.9	56.9	50.3	44.7	40.0
150	79.8	69.2	60.6	53.4	47.4	42.4

Table 7

Universal pressure-viscosity coefficient, reciprocal asymptotic isoviscous pressure and product $\eta_0^{0.69}\alpha_{film}^{0.56}$ for the tris(2-ethylhexyl) trimellitate studied in this work at several temperatures.

T/K	TOTM		
	α_{film} / GPa^{-1}	$\alpha*$/GPa^{-1}	$\eta_0^{0.69}\alpha_{film}^{0.56}$
303.15	20.0	19.5	172.1
313.15	18.6	18.2	111.1
323.15	17.5	17.1	75.7
333.15	16.6	16.2	54.1
343.15	15.8	15.4	40.3
353.15	15.2	14.8	31.0

η_0 is reported in mPa s.

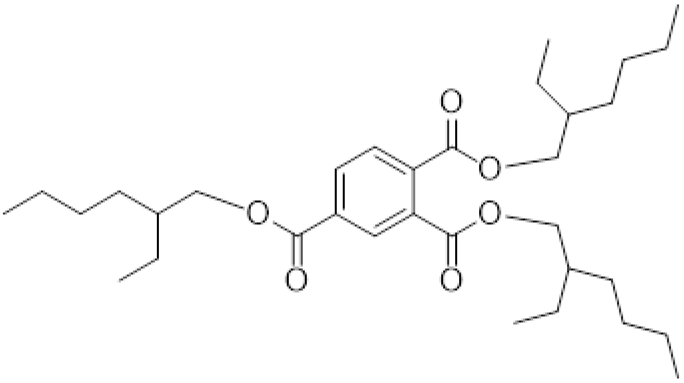

Fig. 1. Chemical structure of tris(2-ethylhexyl) trimellitate (TOTM)

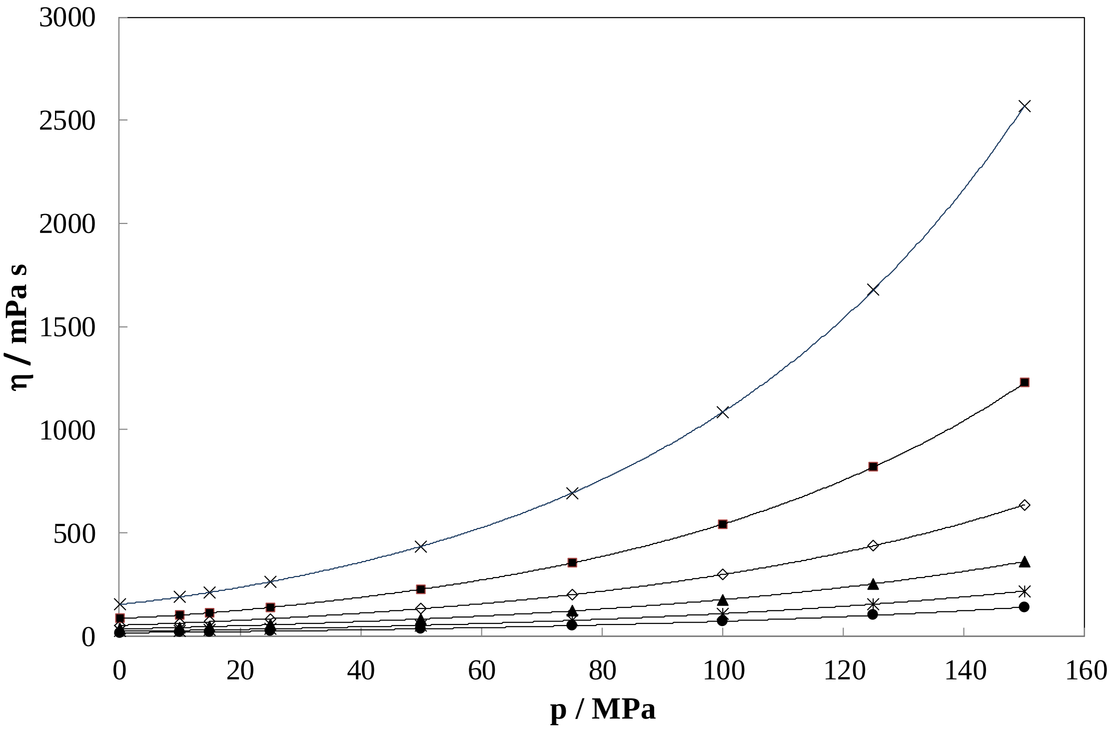

Fig. 2. Experimental viscosity values, η, as a function of pressure for tris(2-ethylhexyl) trimellitate. (×) T = 303.15 K, (■) T = 313.15 K, (◇) T = 323.15 K, (▲) T = 333.15 K, (∗) T = 343.15 K and (●) T = 353.15 K. The solid lines represent the values obtained using equation (4).

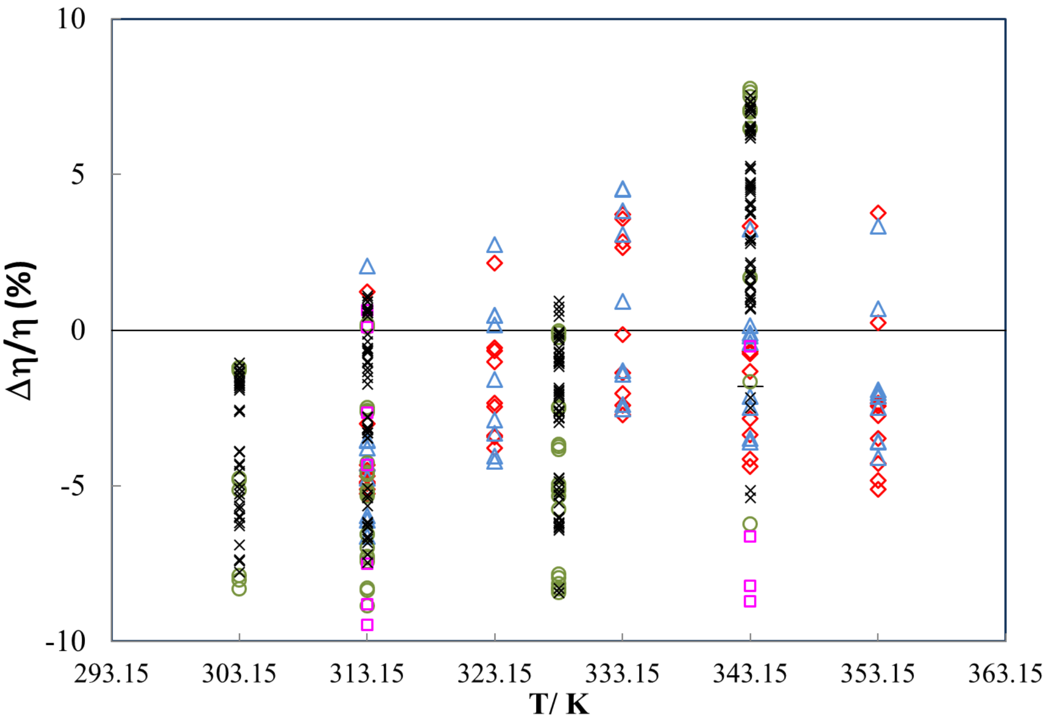

Fig. 3. Relative deviations between the viscosities reported in this work and: (◇) equation (7) of Baled [11]; (△) equation (9) of Baled et al. [11]; (□) Bair et al. [10], (○) Diogo et al. [7] and (×) Diogo et al. [5].

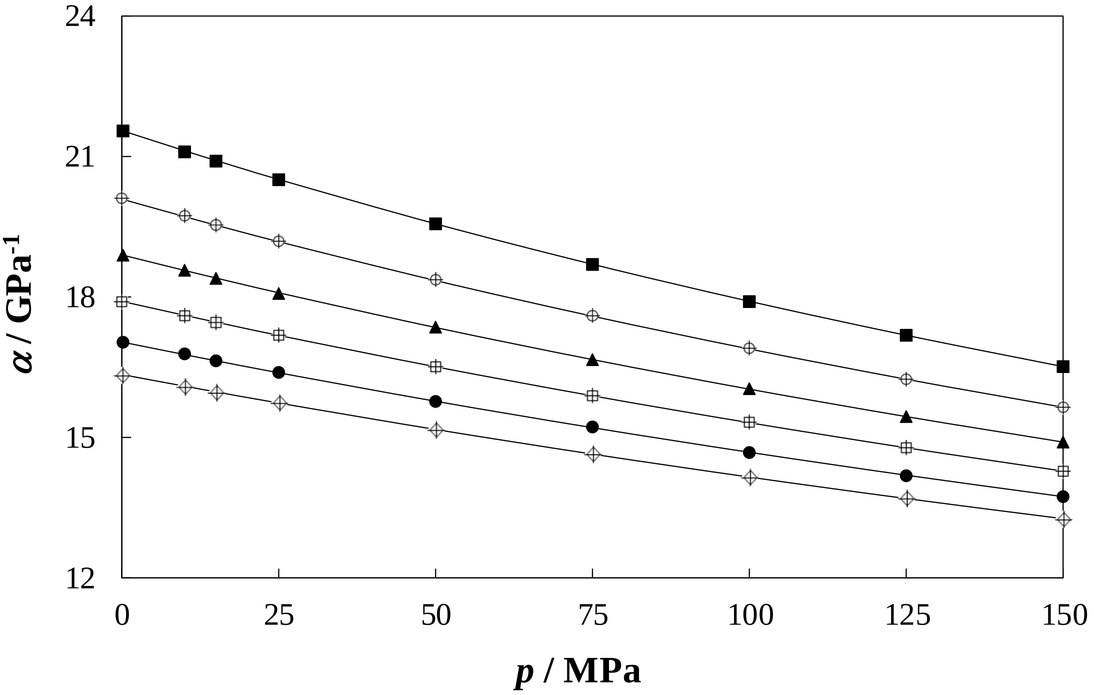

Fig. 4. Local pressure–viscosity coefficient, α, as a function of pressure for tris(2-ethylhexyl) trimellitate (TOTM). (■) T = 303.15 K, (⦶) T = 313.15 K, (▲) T = 323.15 K, (⊞) T = 333.15 K, (●) T = 343.15 K and (✧) T = 353.15 K.

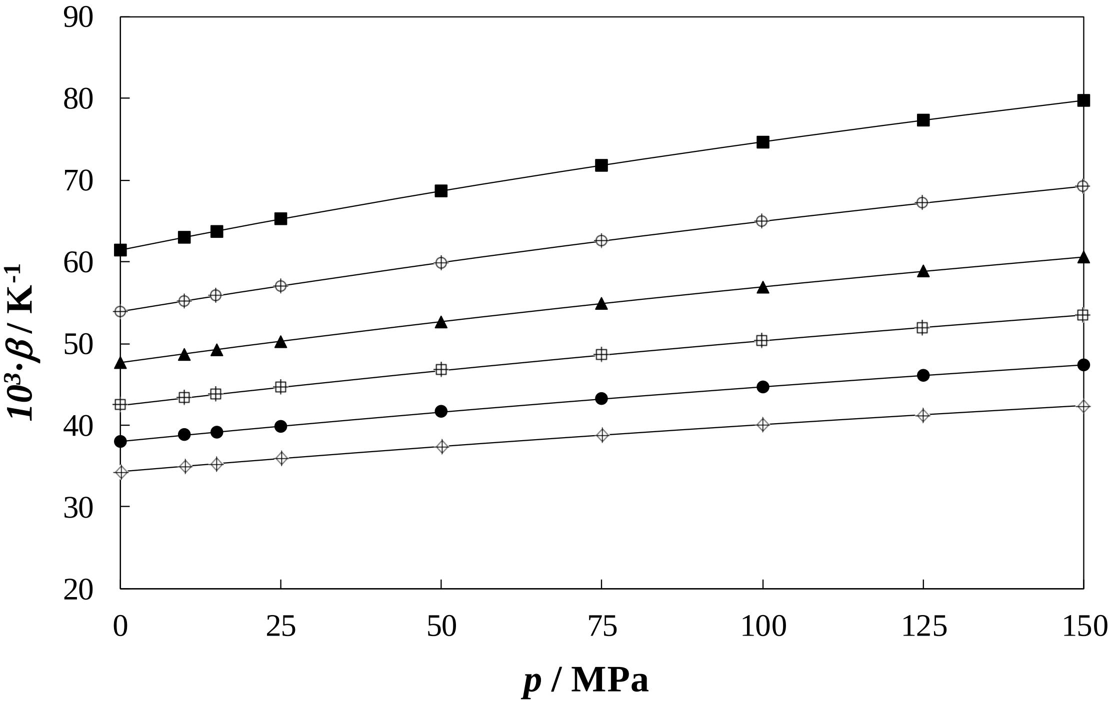

Fig. 5. Local temperature–viscosity coefficient, β, as a function of pressure for tris(2-ethylhexyl) trimellitate (TOTM). (■) T = 303.15 K, (⊕) T = 313.15 K, (▲) T = 323.15 K, (⊞) T = 333.15 K, (●) T = 343.15 K and (◇) T = 353.15 K.

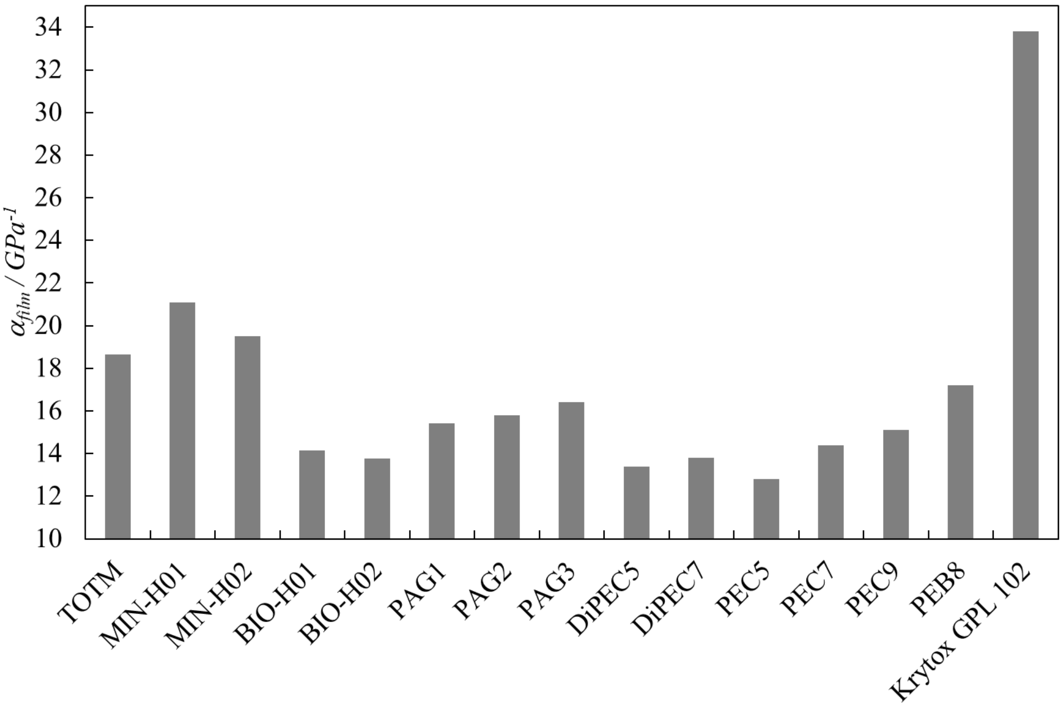

Fig. 6. Universal pressure-viscosity coefficient, α_{film}, at 313.15 K for several fluids: mineral oils (MIN-H01 and MIN-H02 [26]), vegetable oils (BIO-H01 and BIO-H02 [26]), polyalkylene glycols (PAG1, PAG2 and PAG3 [27]), pentaerythritol esters (PEC5, PEC7, PEC9 and PEB8 [27]), dipentaerythritol esters (DiPEC5 and DiPEC7 [27]) and another standard reference fluid (Krytox GPL 102 [10]).

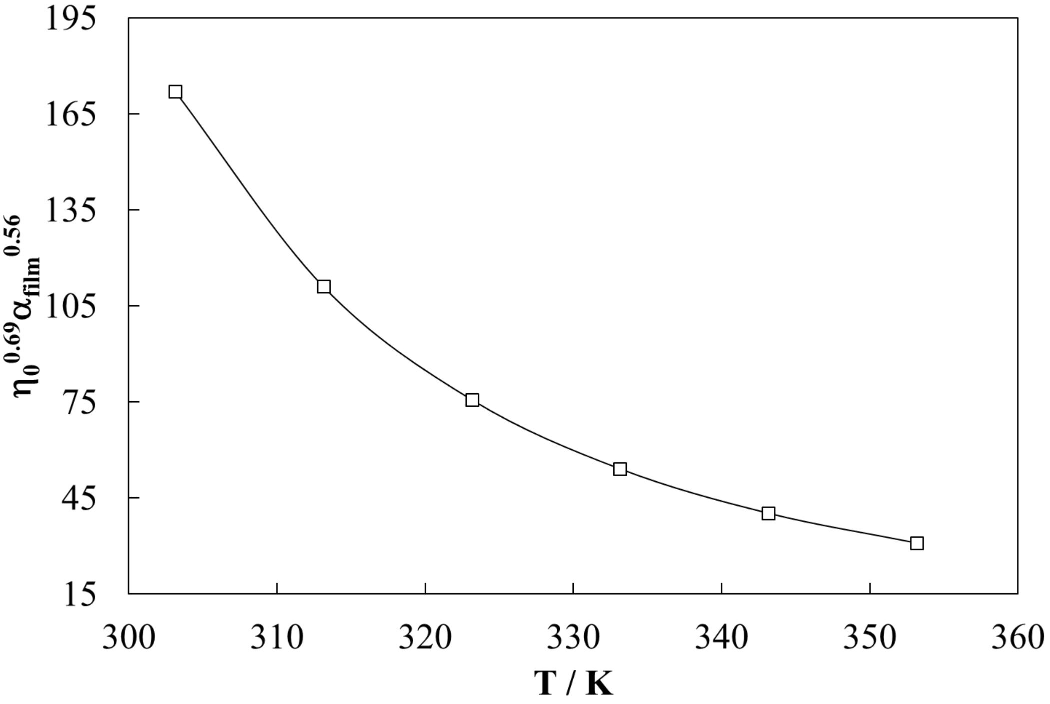

Fig. 7. Film thickness factor, $\eta_0^{0.69}\alpha_{film}^{0.56}$, due to the lubricant for TOTM, as a function of temperature.

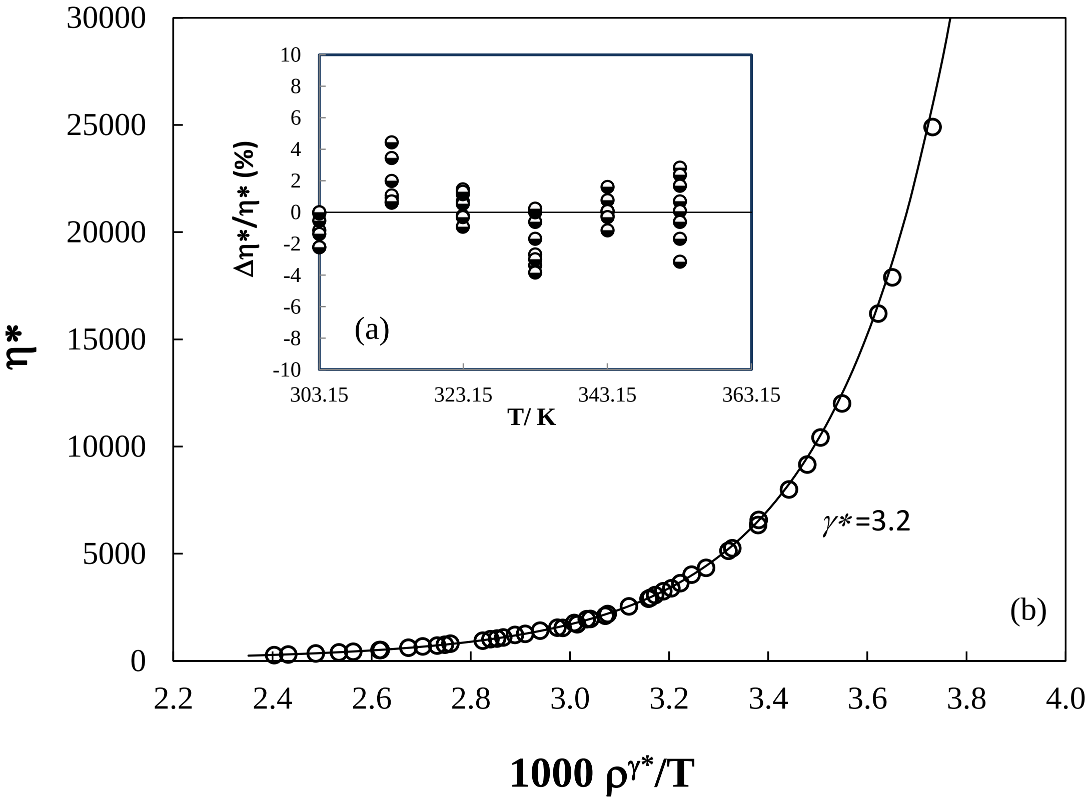

Fig. 8. (a) Relative deviations between the values of Tables 3 and 4 and those obtained with equation 17; (b) reduced viscosity, η^*, of TOTM plotted against the function $1000\rho^{\gamma^*}/T$. The solid line was obtained from equation (17).