

# **Viscosity Measurements for Squalane at High Pressures, to 350 MPa, between 293.15 K and 363.15 K**

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## **ABSTRACT**

Squalane is being recommended as a secondary reference material for viscometry at moderate to high pressure and at moderate viscosity. As part of this work, a correlation has been developed for atmospheric pressure (Comuñas et al, J. Phys. Chem. Ref. Data, 42, 033101, 2013). Here we report new experimental high pressure viscosities for squalane (176 data points obtained between 293.15 and 363.15K, at pressures up to 350 MPa with a maximum viscosity of 745 mPa·s. These have been determined with four different falling-body viscometers as well as a quartz crystal resonator viscometer. A preliminary high pressure viscosity correlation for squalane is proposed, based on our new data. At pressures up to 350 MPa, this correlation provides an absolute average deviation of 1.5 % with a maximum absolute deviation of 8.9 %. Comparison is made between the different instruments. In addition, we have also considered the validity of a thermodynamic scaling model.

*Keywords:* Squalane; Viscosity; High Pressures; Reference material; Thermodynamic scaling

## 1. Introduction

There is a requirement for a reference material for viscosity measurements at moderate to high pressures that can be used for the calibration of viscometers designed for such pressures, both for laboratory and industrial work. To this end, there have been several previous studies that have led to useful, though limited, correlations.

The first is based on one of the commercially available certified viscometer calibration fluids, Cannon S20, which is a mixture of hydrocarbons. Kandil et al. [1] employed both vibrating wire (VW) and falling body (FB) techniques over a temperature range of 273 to 473 K at pressures to 275 MPa with an expanded uncertainty ( $k = 2$ ) of 2.3 % . Both types of viscometer have well-defined and well-verified working equations. This work extended previous measurements by Lundstrom et al. [2] and Sopkov et al. [3] that each had an upper limit of 55 MPa. The atmospheric pressure values used to calibrate the high pressure viscometers derive from the standard viscosity [4] of water at 293.15 K and 0.1 MPa, either directly or indirectly, through the step-up procedure employing a chain of intermediate reference liquids and a series of master capillary viscometers. However, materials such as S20 slowly degrade, due to composition changes caused by evaporation, and so must be used within a specified time, and the absolute atmospheric pressure viscosities of individual lots may differ. It is necessary therefore to assume that the pressure dependence of different lots is the same for the high pressure measurements to be employed as a reference.

The second study proposed diisodecyl phthalate (DIDP) as an interim reference material, and was put forward by the International Association of Transport Properties (<http://transp.eng.auth.gr>) [5]. This is also a careful and critical compilation based on measurements from a range of viscometers of different types (VW, FB, capillary (C) and

surface light scattering (SLS)), but applies to only atmospheric pressure between 288 and 308 K for viscosities between 49 and 171 mPa·s. It has an expanded uncertainty of 2 % ( $k = 2$ ). There are high pressure data [6; 7] available, but these have not been used for a reference correlation as DIDP is not available as pure substance, but only as a complex mixture of isomers (the effect of this is considered to be small, but cannot be determined exactly), and, more seriously, the main manufacturer has ceased production of high purity material.

Other moderately viscous fluids that are available as single isomers, such as di(2-ethylhexyl) sebacate (DEHS), 2-ethylhexyl benzoate (EHB), and bis(2-ethylhexyl) phthalate (DEHP), have also been suggested for use as moderate viscosity reference fluids [8]. Harris [8], and Paredes et al. [9] have reported viscosities at high pressures for these compounds, including a correlation of the literature high pressure data for DEHS in the second study. However, 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 [8; 10]. Consequently, this substance may not meet occupational safety and health (OSH) criteria in certain countries or organizations for use as a reference viscosity standard [8; 11]. Of the other compounds, EHB is quite an expensive material and its viscosities are the lowest among the possible candidates. 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 97 % purity at present.

Given the constraints on the use of S20 and DIDP as moderate viscosity reference materials, and the drawbacks of DEHP, EHB and DEHS, attention has moved to squalane ( $C_{30}H_{62}$ , tetracosane, 2,6,10,15,19,23-hexamethyltetracosane or, for brevity, SQN). Its advantages are that it is moderately viscous, has a wide liquid range and a low vapor pressure, is relatively inexpensive and is available with mole purities above 99 % in a

single isomeric form. As a hydrocarbon, it should be of particular usefulness as a reference material for work on hydrocarbon-based oils under the conditions met in oil-field reserves and on liquids that wet the solid surfaces of a viscometer in a similar way (unlike water). The available experimental data in the literature, together with new measurements from a variety of viscometer types, all at atmospheric pressure, have been critically examined recently and a reference correlation put forward, again under the auspices of IATP [12].

The next stage is to enlarge the available high pressure data. In this work, we have made additional experimental measurements of the viscosity of squalane as a function of temperature and pressure to extend and round out the range of state points to be covered. This has been done using falling body and quartz crystal resonator viscometers in three different laboratories at the Universities of New South Wales (UNSW), Pau (UPPA) and Santiago de Compostela (USC), thus providing a consistency check for the various instruments and techniques, as in the DIDP study [5]. These are all reported here as a single source of data. The data cover the temperature range 293.15 K and 363.15 K, and extend to 350 MPa pressure. A high pressure correlation for squalane, considering these new measurements and all the high pressure data from the literature [8; 13-22] as well as other two sets recently measured in other laboratories, is to be published in a separate work [23]. We will only give a preliminary correlation in this work, based only on our own data, just in order to check the consistency of our new measurements.

## **2. Experimental Section**

The provenance and purity of the three squalane samples (CAS 111-01-3) and some reference fluids, decane (CAS 124-18-5), diisodecyl phthalate sample (CAS 26761-40-0) and Bis(2-ethylhexyl) phthalate (CAS 117-81-7), are provided in Table 1. The

water content of squalane was measured at USC by Karl Fischer analysis, yielding a weight fraction of  $12 \cdot 10^{-6}$ .

A falling body viscometer was used at the University of New South Wales (FB-UNSW). This viscometer has been described previously [24; 25]. In this viscometer, for laminar flow, the viscosity  $\eta$  is related to the sinker's fall time  $\Delta t$ , by the following equation:

$$\eta = \frac{\Delta t (1 - \rho_L / \rho_S)}{A [1 + 2\alpha (T - 298.15 \text{ K})] [1 - 2\beta (p - 0.1 \text{ MPa})/3]} \quad (1)$$

where  $\rho_L$  and  $\rho_S$  are the liquid and sinker densities, respectively,  $A$  is the viscometer constant,  $\alpha$  is the linear expansion coefficient and  $\beta$  is the linear compressibility of the sinker and the tube. The density values  $\rho_L$  needed in equation (1) to determine the viscosities of squalane were calculated as described previously [8]; the density of the sinker at each temperature and pressure was determined using the equation given by Dymond et al. [26].

The viscometer constant  $A$  was determined by calibration with Cannon Instrument Company oils (N100, S200 and N4000, 6.0 mm sinker; N100, plus toluene and octane, 6.3 mm sinker [8]) at atmospheric pressure between 298.15 and 353.15 K. It is found to be independent of temperature and viscosity, and assumed independent of pressure, any pressure effect on the sinker clearance being taken into account by the compressibility term in the denominator of equation (1). The measurements have been performed over the temperature interval 313.15 to 363.15 K and up to 349.8 MPa. The expanded uncertainties (coverage factor  $k = 2$ ) claimed [8] are 0.2 MPa for the pressure, 0.02 K for the temperature and the expanded uncertainty of the viscosity measurements performed with this viscometer and this procedure is 2.3 % [1].

The falling body viscometer of the University of Pau (FB-UPPA) was described previously [27]. The uncertainty in pressure, measured with a HBM P3M transducer, is  $\pm 0.1$  % of the full scale (200 MPa) and that of the temperature, measured with an AOIP PHP602 thermometer, is  $\pm 0.05$  K. The fall time is measured with a stop watch and is reproducible to better than 1 %. The viscosity was determined from the following relation:

$$\eta(p, T) = K(p, T) [\rho_S - \rho_L] \Delta t \quad (2)$$

where  $\rho_S$  is the density of the sinker,  $\rho_L$  the density of the liquid at pressure  $p$  and temperature  $T$ ,  $\Delta t$  the fall time and  $K(p, T)$  is a calibration parameter that takes into account the geometry of the apparatus and which is taken to be function of  $p$  and  $T$ . Very often,  $\rho_S$  is supposed independent of  $p$  and  $T$  for the intervals of pressure and temperature considered. This is the case for this study. A sinker with density  $7.717 \text{ g}\cdot\text{cm}^{-3}$  was used. The density values  $\rho_L$  needed in equation (2) for the viscosities of squalane have been taken from Ciotta et al. [15]

The term  $K(p, T)$  is usually determined using a reference compound of known viscosity. It is best to use a reference compound where the viscosity is not too different from that of the fluid studied, but this is not always possible, as in the present case. An alternative is to use a ‘self-reference’ method. Measuring precisely the viscosity at atmospheric pressure with a capillary viscometer [12], it is easy to determine  $K(0.1 \text{ MPa}, T)$ :

$$K(0.1 \text{ MPa}, T) = \frac{\eta_{\text{squalane}}(0.1 \text{ MPa}, T)}{[\rho_S - \rho_{\text{squalane}}(0.1 \text{ MPa}, T)] \Delta t} \quad (3)$$

Then it is assumed that the pressure has a limited influence on  $K$ . Strictly speaking this is untrue but we consider that any deformations in the experimental cell remain very small as the fluid is located both inside and outside the inner tube of the measuring cell. We have constrained our study to  $p < 200$  MPa. Under this condition, we

used  $K(p, T) \approx K(0.1 \text{ MPa}, T)$ . The expanded uncertainty ( $k = 2$ ) of the measured viscosity is estimated at  $\pm 3.5 \%$  with this falling-body viscometer and procedure for pressures below 200 MPa, between 303.15 and 348.15 K.

The quartz crystal resonator viscometer of the University of Pau (QCR-UPPA) has recently been developed by Daridon et al. [28] The pressure is measured with a gauge (Kulite HEM-375 M, uncertainty 0.05 MPa) inserted into the cell. 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. The viscosity is determined from the damping of the quartz vibrations for different overtones and using the ratio  $c_{exp}$  between the half-band half-width and the overtone number through the relation:

$$\eta = \frac{\pi f_0}{\rho_L C_m^2} \left( \frac{c_{exp}}{1 + R_{interface}} \right)^2 \quad (4)$$

where  $f_0$  is the resonance frequency,  $\rho_L$  is the density of the liquid,  $C_m$  is the Sauerbrey coefficient [29], and finally  $R_{interface}$  is a coefficient related to the quartz surface morphology that appears to be independent of pressure [30]. Two methods have been used in this work to obtain  $R_{interface}$  by calibration and thus to determine the viscosity of squalane under pressure from 293.15 to 333.15 K and up to 80 MPa. One is based on the estimation of the parameter  $R_{interface}$  by using decane as reference liquid (QCR-UPPA 1) and the second one consists in using the viscosities of squalane at atmospheric pressure as a self-reference (QCR-UPPA 2). We have found only small differences between these methods, with an average absolute deviation of 0.5 % and a maximum deviation of 1.1 %, both below the expanded uncertainty estimated to be 4% ( $k = 2$ ).

At the University of Santiago de Compostela two falling body viscometers (FB-USC VisLPT1 and FB-USC VisLPT2) were employed [31; 32] with maximum working pressures of 150 and 250 MPa respectively. In both USC viscometers, the temperature is regulated using a circulating thermostat and is measured with thermocouples located inside the cells and in contact with the sample with an uncertainty of  $\pm 0.5$  K. In the VisLPT1 instrument, the sample is compressed by means of a hydraulic compressor and in the VisLPT2 instrument by a pneumatic pump. The pressure is measured by digital transducers with an accuracy of  $\pm 0.2$  MPa in both viscometers.

The measuring principle is based on the relationship between viscosity and the time ( $\Delta t$ ) that a solid takes to fall through a viscous fluid once it has reached its terminal velocity. The viscosity was determined from the following expression:

$$\eta = a + b(\Delta\rho\Delta t) + c(\Delta\rho\Delta t)^2 \quad (5)$$

where  $a$ ,  $b$  and  $c$  are calibration parameters and  $\Delta\rho = \rho_S - \rho_L$  is the difference between the density of the sinker and that of the liquid under study. Both USC viscometers were calibrated using DIDP and DEHP as reference fluids and the measurements were performed from 313.15 to 343.15 K for VisLPT1, 313.15 to 363.15 K for VisLPT2, and at pressures reaching 150 and 250 MPa for the VisLPT1 and VisLPT2 instruments respectively. The viscosities of these fluids were taken from the correlations given by Harris [8] and Peleties and Trusler [33] for DIDP, and by Harris [8] for DEHP. The densities of DIDP and DEHP have been obtained from Peleties et al. [34] and from Harris [8], respectively. The density values  $\rho_L$  needed in equation (6) to determine the viscosities of squalane have been taken from Ciotta et al. [15]. A sinker with a density of  $7.695 \text{ g}\cdot\text{cm}^{-3}$  was used in the VisLPT1 apparatus and one with a density of  $7.738 \text{ g}\cdot\text{cm}^{-3}$  in VisLPT2. Note that for relations (1), (3) and (6) an error of 1 % in  $\rho_L$  (i.e. a very bad estimation of the density of the fluid) implies a relative error less than 0.2 % in  $\Delta\rho$  ( $\rho_S$  is around 7.5

$\text{g}\cdot\text{cm}^{-3}$  and the maximum squalane density for our experiments was  $0.892 \text{ g}\cdot\text{cm}^{-3}$ ). We have estimated with these devices and this procedure an expanded uncertainty ( $k = 2$ ) up to 5 % for both VisLPT1 and VisLPT2 at the highest pressures.

For the falling-body viscometers, three working equations, (1), (2) and (5), have been used in this work. This allows comparison of three different designs. The reader should be aware that there is no complete theory (valid for all experimental conditions) for this type of device, which should never be used in absolute mode. For ideal laminar flow, the theory predicts  $\eta = K\Delta t\Delta\rho$ . Nevertheless, in practice  $k$  is not a constant and varies slightly owing to several effects, in particular linked to the flow around the sinker and effects linked to the deformation of the measuring cell and the sinker due to temperature and pressure changes. Thus it is always necessary to perform a calibration. For dense fluids a linear dependence of  $\eta$  with the product ( $\Delta t\cdot\Delta\rho$ ) can be accepted as a very good approximation (equations (1) and (2)). In equation (1), deformation effects are taken into account with the expansion coefficient ( $\alpha$ ) of  $1.6\cdot 10^{-5} \text{ K}^{-1}$  and the compressibility coefficient ( $\beta$ ) of  $2\cdot 10^{-6} \text{ MPa}^{-1}$  for the material in which the cell and sinker have been built. In equation (2), for the pressure range considered ( $p < 200 \text{ MPa}$ ), the deformation due to pressure is neglected owing to the design of the measuring cell (with two tubes the pressure on the internal wall of the measuring tube is the same than the pressure on the external wall), whereas the influence of temperature and other effects are supposed included in the calibration of  $k$  with temperature (equation (3)). Note that for equation (1), the correction factor for a temperature interval of 50 K is  $2\alpha\Delta T = 1.6\cdot 10^{-3}$ , and the correction factor for a pressure interval of 200 MPa is  $2\beta\Delta p = 8\cdot 10^{-4}$  as the sinker and the tube are made with the same steel material. The following discussion will emphasize that this equation gives viscosity values similar to the values determined by the other methods, taking account their own accuracy. For the apparatus described by

equation (2), which does not include a pressure correction, it is necessary to use a calibrating fluid, and it is known that the best option is to use a reference fluid with similar viscosity to the targeted fluid in the same  $(p,T)$  conditions. For self-reference method, where  $\eta(0.1 \text{ MPa}, T)$  is the reference value, the reader should be aware that it is consequently necessary to do experiments with a ratio  $\eta(p,T)/\eta(0.1 \text{ MPa}, T)$  that is not too high so that the targeted viscosity value is not too far from the reference value. The comparison with the other methods has shown that for the UPPA falling body viscometer (used here with self-reference method), the limiting threshold of this viscosity ratio is around 25. Above that value, the method yields increased deviations from other methods, which seem to increase with the viscosity ratio (at 200 MPa and 303.15 K the ratio is 36 using the viscosity determined by the other methods). Equation (5), which is slightly different, can be written as  $\eta = a + b \cdot \Delta t \cdot \Delta \rho (1 + b' \Delta t \Delta \rho)$ . Inclusion of the constant  $a$  allows a better determination of smaller viscosities [35]. Besides, it has been also proposed [36] that  $k$  can be a function of  $(\Delta t \Delta \rho)$ . In equation (5), USC has generalized these ideas to even high viscosity and the constant  $a$  and the first order correction factor  $(1 + b' \Delta t \Delta \rho)$  have been used. Calibration with several fluids ensures that there is no divergence over the pressure and temperature ranges of the calibration, i.e. the correction factor  $(1 + b' \Delta t \Delta \rho)$  stays close to 1 even when the viscosity (i.e.  $\Delta t$ ) is high. In such a way it is hoped that all the effects are taken into account. With equation (5), the calibration is made using two calibrating fluids under the same  $(p,T)$  conditions applied to the unknown fluid. Comparison with the values obtained by the other methods has shown that the results obtained with this method are in good agreement. In such a calibration method, the value of the ratio  $\eta(p,T)/\eta(0.1 \text{ MPa}, T)$  is not critical, because the calibration method for VisLTP1 and VisLTP2 uses fluids which are under the same  $(p,T)$  conditions as the unknown fluid (using reference fluids with similar viscosities). Finally, we will see in the

next section of the article that the absolute average deviations for these experimental sets are less than the experimental uncertainties, a result that shows the consistency of our measurements.

### 3. Results and Discussion

The viscosity measured with the instruments described above are reported in Tables 2 and 3 for pressures up to 350 MPa and from 293.15 K to 363.15 K. The viscosity data for squalane were correlated with a modified VFT equation which has eight parameters and employs a third degree polynomial in the pressure as follows:

$$\eta = A \exp \left( a_1 \Delta p + a_2 \Delta p^2 + \frac{B + b_1 \Delta p + b_2 \Delta p^2 + b_3 \Delta p^3}{T - C} \right) \quad (6)$$

where  $\Delta p = p - p_{\text{ref}}$ . This equation corresponds to a small modification of a relation employed recently by Harris[8] (through the use of  $\Delta p$  rather than  $p$ ). Ducoulombier et al. [37] and Paredes et al. [6; 9] have used very similar equations in the past. In equation (6) we use 0.1 MPa as the reference pressure. Therefore when  $p$  is also equal to 0.1 MPa this equation collapses to:

$$\eta = A \exp \left( \frac{B}{T - C} \right) \quad (7)$$

The Vogel-Fulcher-Tammann (VFT) form, equation (7), has been used recently by Comuñas et al. [12] in proposing a reference correlation for the viscosity of squalane at 0.1 MPa. This correlation is valid from 273 K to 373 K and describes selected literature viscosity values [13; 14; 16-20; 38-45] with an average absolute percent deviation of 0.67 %. Hence, the parameters  $A$ ,  $B$  and  $C$  we use in the present work in equation (6) are taken for this reference correlation recently published ( $A = 0.06266$ ,  $B = 808$  K and  $C = 165.9$

K) and are not further adjusted. This leaves the five parameters,  $a_i$  and  $b_j$ , to be determined from the fit to the viscosity measurements for high pressure.

Note also that in equation (6)  $\ln(\eta)$  is a linear function of the parameters  $a_i$  and  $b_j$  as  $C$  is held constant. That means it is possible to get an optimal set of five parameters that

minimises the objective function  $S = \sum_1^N (\ln(\eta_{calc}) - \ln(\eta_{exp}))^2 = \sum_1^N (\ln(\eta_{calc}/\eta_{exp}))^2$ . The

software used for the regression procedures were Excel (Microsoft) and Statistica (Statsoft). To describe the goodness of the fits performed in this article we have used the absolute average percent deviation AAD, Bias and maximum absolute percent deviation MD defined in previous works [12; 46]. The values of the absolute average percent deviation AAD, Bias and maximum absolute percent deviation MD have been rounded to 0.1 when the values are higher than 1 %, otherwise to 0.01. In the Tables 4 to 6, the parameter values have been rounded to 6 significant digits in order not to introduce changes in the calculated viscosities linked to the rounding of the parameters in the calculations.

Keeping  $A$ ,  $B$  and  $C$  constant, the five coefficients  $a_i$  and  $b_j$  of equation (6) have been obtained by minimising the AAD on viscosities (not the function  $S$ ) at pressures below 350 MPa (a total of 176 experimental values from 293.15 to 363.15 K and from 4.4 to 745 mPa·s at pressures higher than 0.1 MPa). The AAD obtained is 1.5 %, the Bias is -0.15 % and the maximum deviation is 8.9 %, which occurs for an experimental value of 16.8 mPa·s at 313.15 K and 10 MPa measured in the FB-USCVisLTP 1.

Table 4 shows the parameters and the total AAD, Bias, MD. Table 5 gives the correlation results for each set of data. We note that for all the different sets of viscosity values reported in this work, the AAD is smaller than the experimental uncertainty. Note also that for each viscosity set the maximum relative absolute deviation is no more than

four times the claimed uncertainty. From a total of 176 data points, there are only six with absolute relative deviation  $>5\%$  as can be seen in Figures 1 and 2. All this emphasizes the good consistency of the viscosity measurements performed in this work with the various instruments and techniques. For the UPPA falling body viscometer, the tendency is that deviation increases when the ratio  $\eta(p,T)/\eta(0.1\text{ MPa},T)$  becomes important (low temperature and high pressure). Hence, with this self-reference method, we have kept only the viscosity values such that  $\eta(p,T)/\eta(0.1\text{ MPa},T)$  stays below 25 (at 303.15 K, there is no experimental determination above 160 MPa). Table 5 shows that there is no real difference between the two sets of values obtained with the quartz crystal resonator (calibration method with either decane or by self-referencing). This is due to the fact that with this device the maximum pressure is only 81 MPa, with not too high a viscosity at the lowest temperature, around 180 mPa·s.

#### 4. Scaling of reduced viscosity

Some years ago it was shown [47] that the relaxation times,  $\tau$ , for various glass-forming liquids and polymers could be super-positioned on a single master-curve when expressed as a function of  $TV^\gamma$  (where  $V$  is the specific volume,  $1/\rho$ , and  $\gamma$  is a constant, characteristic of the material). In other words  $\tau$  is found to be a unique function of  $TV^\gamma$ :

$$\tau(T,V) = f(TV^\gamma) \quad (8)$$

It is worthwhile to mention here that this scaling was first applied in 1975 to the reduced excess viscosity of soft-sphere and Lennard-Jones fluids by Ashurst and Hoover [48]. Roland et al. [49] extended this so-called “thermodynamic scaling” to the viscosity of a number of real fluids. For a given compound the viscosity  $\eta$  is a functional of the quantity  $TV^\gamma$ :

$$\eta(T, V) = \eta(T, \rho) = f(TV^\gamma) = f(T\rho^{-\gamma}) \quad (9)$$

where  $f$  is also an unknown function (at least up to now). The parameter  $\gamma$  reflects the steepness of the repulsion between two molecules [47-49]. It links thermodynamics to a given transport property (here the viscosity) and quantifies the relative influence of the volume and temperature on the dynamic behaviour of compounds. In practice it is obtained graphically from the super-positioning of isotherms for  $\ln(\eta)$  plotted against  $TV^\gamma$ , with  $\gamma$  chosen such that these form a single curve, or by an equivalent least squares procedure for an arbitrary, but convenient, function  $f$ , such as a polynomial in  $TV^\gamma$ . Roland et al. [49] have confirmed equation (9) for several liquids. It has been found that  $\gamma$  is larger for van der Waals fluids (e.g.  $\gamma = 8$  for octane) than for ionic liquids (e.g.  $\gamma = 2.25$  for 1-methyl-3-octylimidazolium tetrafluoroborate). On the other hand, it has been observed that the superposition fails for some strongly hydrogen-bonded materials, such as water [49; 50]. Equation (9) has been more deeply examined by other authors. In particular, in articles by Fandiño et al. [51], Pensado et al. [50] and López et al. [52] the superposition is very clearly observed for several pentaerythritol ester lubricants, for linear and branching alkanes, polar liquids, ionic liquids, and alcohols. The values of the  $\gamma$  exponent for the fluids analyzed by Pensado et al. [50] range from 1.45 for ethanol to 13 for *n*-hexane. Very recently, using the residual reduced viscosity, Galliero et al. [53] have found that the thermodynamic scaling scheme is also well respected by the Lennard-Jones chain fluid over a wide range of thermodynamic conditions. In addition, thermodynamic scaling has been shown [53; 54] to hold for simple real nonpolar fluids, such as argon, methane, *n*-butane, *n*-decane and sulphur hexafluoride where accurate viscosity data are available.

Although several authors [50; 55; 56] have proposed expressions for the function  $f(TV)$  in equation (9) for non-reduced quantities, to our knowledge there are no studies on the form of  $f$  for reduced quantities. The use of reduced transport properties is an alternative procedure based on the behaviour of the liquids which obey the inverse potential law and on the new concept of “isomorphic” curves in the phase diagram [57; 58]. Again, the fitting should be done in such a way that the reduced data collapse onto a single master curve. Firstly, we define the following reduced quantities:

$$\eta_r = \frac{\eta_{exp}}{\eta^*}, \quad T_r = \frac{T_{exp}}{T_c}, \quad \rho_r = \frac{\rho_{exp}}{\rho_c} \quad \text{with} \quad \eta^* = \rho^{2/3} \sqrt{RT} / M^{1/6} \quad (10)$$

where  $R$  is the gas constant,  $M$  the molar mass,  $T_c$  the critical temperature and  $\rho_c$  the critical density. We define the thermodynamic quantity  $x_r$  as  $(T_r / \rho_r^\gamma)$ . We have fitted the reduced viscosities determined from our new data set for squalane using a completely arbitrary empirical function that appears to behave satisfactorily, namely:

$$\eta_r = \exp\left(a_0 + a_1 / x_r + a_2 / x_r^2 + a_3 / x_r^3\right) \quad (11)$$

The experimental critical temperature [59] of squalane is  $T_c = 822$  K, the critical density from Monte Carlo simulations [60] is estimated at  $\rho_c = 228$  kg·m<sup>-3</sup>, and the molar mass  $M = 0.42283$  kg·mol<sup>-1</sup>. The density data, necessary for  $x_r$ , were calculated from the correlation given by Ciotta et al. [15] but this correlation has been established only for the temperature range  $303.15 < T/K < 448.25$  and for pressures below 176 MPa. To avoid density extrapolation, the database has been reduced in consequence to these pressure and temperature ranges. The number of data points from Tables 2 and 3 remaining for the scaling fit is 134 (with viscosities lying between 3.1 and 422.5 mPa·s). Furthermore, we have also used viscosity data previously reported by our three laboratories [12] for 0.1 MPa within the Ciotta temperature interval (27 points). Therefore the reduced database contains a total of 161 values. Equation (11) was used to determine the coefficient  $\gamma$  by

minimizing the AAD( $\ln(\eta_r)$  is linear function of the  $a_i$  but is not linear function of  $\gamma$ ). The parameters  $a_i$  and the coefficient  $\gamma$  are given in Table 6. The fit yielded AAD = 1.5 %, Bias= -0.11 % and a MD =9.3 %, found for the FB-USC VisLPT1 experimental value at 313.15 K and 10 MPa ( $\eta_{exp} = 16.8$  mPa·s) Figure 3 shows the variation of the deviations against pressure. From a total of 161 data points, there are only seven with an absolute relative deviation above 5 %. Again good agreement for the data of this work is consistently obtained as can be seen in Table 7. The value of  $\gamma$  obtained from this procedure is practically 4.15, very close to that found by Roland et al. [49] and Harris [8] for non-reduced transport properties ( $\gamma=4.2$  and 4.16, respectively) and also to that found by Bair and Laesecke [56] ( $\gamma = 3.92$ ) who reduced only the volume, not the viscosity. Figure 4 very clearly shows there is indeed a single master curve of  $\eta_r(x_r)$  and that the scaling relation of Roland et al. [47; 49] can be used to determine the volume and temperature dependence of the reduced viscosity. Note that the curve in Figure 4 is independent of the form of equation (11), used for the fitting. The curve depends only on the  $\gamma$  value, and it shows that  $\gamma \approx 4.15$  is really a good estimate in order to get a master curve. It is worth mentioning that in fact, it is also possible to determine  $\gamma$  without any information on the function  $f$ . Considering equation 9, it follows that on an isoviscous line, the product  $T\rho^\gamma$  has to be constant, which leads to  $\ln(T) = A + \gamma \ln(\rho)$  (likewise for the reduced quantities). Thus, drawing  $\ln(T)$  versus  $\ln(\rho)$  at isoviscous conditions allows the determination of  $\gamma$  from the slope of the line. This looks like a rather simple method, but this approach presents its own difficulties because it is quite impossible to get such isoviscous data directly from experiments. In practice, it is necessary to draw various isobaric (or isothermal) viscosity lines, then choose a fixed viscosity value and keep track of the corresponding  $(p,T)$  values, so as to be able to calculate, the density of the liquid at those  $(p,T)$  states with a suitable density correlation equation. In addition, there creates

an additional uncertainty at each step. Furthermore, this procedure should be carried out for several viscosity values and the number of points needs to be sufficient along each viscosity line for the calculation to be significant. Note that in using a closely related method (Figure 5 of Bohling *et al.* [61]), it seems that for some liquids there are deviations from single power-law scaling such as equation (9);  $\gamma$  increases with density. However, these authors insist on the fact that the power law density scaling is a useful approximation to isomorph scaling when only moderate density changes are considered. This is the case for our scaling study where the density varies by only around 12 % (between 758 and 863 kg.m<sup>-3</sup>). Assuming equation 9, we get for the viscosity AAD = 1.5% (around the experimental uncertainty) and MD = 9.3%. These low values seem to indicate, that at least in our density interval, the power law density scaling is valid and  $\gamma$  is constant.

#### **4. Conclusions**

In this paper we report data and preliminary correlation for the viscosity of squalane over a range of temperatures, pressures and viscosities. We have made new measurements in our three laboratories using falling body and quartz resonator viscometers. In particular, that has allowed us to check the validity of the different calibration procedures for falling body viscometers. These values were satisfactorily correlated as function of temperature and pressure by using a modified VFT equation (5 adjustable parameters) with an average absolute relative deviation of 1.5 %. Finally we have used thermodynamic scaling to determine the scaling parameter,  $\gamma$ , which is related to the steepness of the repulsive part of the intermolecular potential. This model was confirmed only for pressures below 176 MPa due to the constraints of the available

equation of state. A value of  $\gamma$  around 4.15 was obtained, consistent with earlier estimates in the literature.

## **Acknowledgments**

We are grateful to our colleagues from the International Association for Transport Properties for helpful discussions. This work was supported by Spanish Ministry of Science and Innovation and the UE FEDER Program under projects CTQ2011-2395 and PSE-420000-2008-4.

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**TABLE 1**

Liquids used in this work.

IUPAC Name	Lot number	Supplier	Mole Fraction Purity
2,6,10,15,19,23-hexamethyltetracosane (Squalane)	1418796	Sigma Aldrich (Fluka)	> 0.990 <sup>a</sup>
Decane	17230LC-195	Sigma Aldrich	0.994
Bis(8-methylnonyl) phthalate (Diisodecyl phthalate)	K22132622	Merck	0.998 <sup>a</sup>
Bis(2-ethylhexyl) phthalate	S42805-258	Sigma Aldrich	0.997 <sup>a</sup>

<sup>a</sup>Gas chromatographic analysis

**TABLE 2**

Experimental viscosities,  $\eta$ /mPa·s, of squalane at high pressures, obtained with falling body viscometers.

$T/K$	$p$ /MPa	$\eta$ /mPa·s	$T/K$	$p$ /MPa	$\eta$ /mPa·s
<i>FB-UNSW<sup>a</sup></i>					
338.15	50.6	15.56	363.15	21.0	5.15
338.15	102.8	32.94	363.15	30.9	5.97
338.15	150.2	60.90	363.15	40.7	6.84
338.15	198.4	108.9	363.15	50.6	7.82
338.15	249.7	194.0	363.15	60.6	8.94
338.15	272.7	243.8	363.15	70.7	10.18
338.15	299.8	327.6	363.15	80.6	11.49
338.15	349.2	538.5	363.15	91.0	13.06
338.15	349.2	531.0	363.15	100.0	14.59
348.15	198.3	70.83	363.15	120.4	18.36
348.15	200.4	72.63	363.15	150.3	25.56
348.15	300.6	202.9	363.15	200.2	42.82
348.15	349.8	327.6	363.15	225.6	55.03
363.15	10.2	4.36	363.15	246.9	66.23
<i>FB-UPPA<sup>b</sup></i>					
303.15	20	34.78	323.15	140	102.35
303.15	40	51.64	323.15	160	135.10
303.15	60	74.96	323.15	180	175.94
303.15	80	107.09	323.15	200	228.18
303.15	100	146.47	348.15	20	7.45
303.15	120	210.53	348.15	40	10.15
303.15	140	305.40	348.15	60	13.51
303.15	160	422.48	348.15	80	17.79
323.15	20	15.77	348.15	100	23.08
323.15	40	22.36	348.15	120	29.61
323.15	60	31.17	348.15	140	37.63
323.15	80	42.71	348.15	160	48.09
323.15	100	57.75	348.15	180	60.38
323.15	120	77.38	348.15	200	74.91
<i>FB-USC VisLPT1<sup>c</sup></i>					
313.15	10	16.8	343.15	10	7.3
313.15	15	18.9	343.15	15	8.0
313.15	25	23.8	343.15	25	9.4
313.15	50	39.2	343.15	50	13.6
313.15	75	61.2	343.15	75	19.2
313.15	100	92.3	343.15	100	26.5
313.15	125	136.4	343.15	125	36.2
313.15	150	199.0	343.15	150	49.1
<i>FB-USC VisLPT2<sup>d</sup></i>					
313.15	50	36.3	343.15	150	52.0
313.15	75	59.6	343.15	175	69.9
313.15	100	91.3	343.15	200	92.8

313.15	125	134.8	343.15	225	122.1
313.15	150	194.1	343.15	250	159.6
313.15	175	275.3	363.15	100	14.2
313.15	200	386.2	363.15	125	19.9
313.15	225	537.7	363.15	150	26.8
313.15	250	744.7	363.15	175	35.1
343.15	75	18.7	363.15	200	45.0
343.15	100	27.2	363.15	225	56.7
343.15	125	38.1	363.15	250	70.4

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<sup>a</sup>Uncertainties:  $u(T) = 0.02$  K,  $u(p) = 0.2$  MPa and  $U(\eta) = 2.3\%$  ( $k=2$ ).

<sup>b</sup>Uncertainties:  $u(T) = 0.05$  K,  $u(p) = 0.2$  MPa and  $U(\eta) = 3.5\%$  ( $k=2$ ).

<sup>c</sup>Uncertainties:  $u(T) = 0.5$  K,  $u(p) = 0.2$  MPa and  $U(\eta) = 5\%$  ( $k=2$ ).

<sup>d</sup>Uncertainties:  $u(T) = 0.5$  K,  $u(p) = 0.2$  MPa and  $U(\eta) = 5\%$  ( $k=2$ ).

**TABLE 3**

Experimental viscosities,  $\eta/\text{mPa}\cdot\text{s}$ , of squalane at high pressures, obtained with a quartz resonator viscometer.

$T/\text{K}$	$p/\text{MPa}$	$\eta/\text{mPa}\cdot\text{s}$	$T/\text{K}$	$p/\text{MPa}$	$\eta/\text{mPa}\cdot\text{s}$
<i>QCR-UPPA 1</i>					
293.15	10.22	45.8	303.15	11.30	28.6
293.15	20.25	57.9	303.15	19.90	34.1
293.15	30.09	70.8	303.15	31.40	43.9
293.15	40.10	87.0	303.15	40.60	53.0
293.15	50.07	108.1	303.15	50.90	64.7
293.15	60.06	130.0	303.15	60.00	78.3
293.15	71.00	160.4	303.15	71.70	94.7
293.15	80.60	180.6	303.15	80.00	107.8
313.15	10.11	18.2	323.15	10.25	12.8
313.15	20.17	22.4	323.15	20.34	15.5
313.15	29.62	26.6	323.15	30.17	18.4
313.15	40.55	32.5	323.15	40.16	21.8
313.15	49.65	38.5	323.15	50.13	25.8
313.15	60.50	47.0	323.15	60.11	30.8
313.15	70.40	55.9	323.15	70.12	36.2
313.15	80.67	66.4	323.15	80.06	43.0
333.15	9.16	9.0	333.15	49.34	17.7
333.15	19.90	10.9	333.15	60.99	21.4
333.15	30.24	13.0	333.15	70.28	25.0
333.15	40.00	15.3	333.15	80.90	28.5
<i>QCR-UPPA 2</i>					
293.15	10.22	46.2	303.15	11.30	28.5
293.15	20.25	58.5	303.15	19.90	34.0
293.15	30.09	71.5	303.15	31.40	43.8
293.15	40.10	87.9	303.15	40.60	52.9
293.15	50.07	109.2	303.15	50.90	64.6
293.15	60.06	131.3	303.15	60.00	78.1
293.15	71.00	162.1	303.15	71.70	94.5
293.15	80.60	182.4	303.15	80.00	107.5
313.15	10.11	18.3	323.15	10.25	12.7
313.15	20.17	22.6	323.15	20.34	15.5
313.15	29.62	26.9	323.15	30.17	18.4
313.15	40.55	32.8	323.15	40.16	21.8
313.15	49.65	38.8	323.15	50.13	25.8
313.15	60.50	47.4	323.15	60.11	30.8
313.15	70.40	56.4	323.15	70.12	36.2
313.15	80.67	66.9	323.15	80.06	43.0
333.15	9.16	9.0	333.15	49.34	17.7
333.15	19.90	10.9	333.15	60.99	21.4
333.15	30.24	13.1	333.15	70.28	25.0
333.15	40.00	15.3	333.15	80.90	28.6

Uncertainties:  $u(T) = 0.1 \text{ K}$ ,  $u(p) = 0.05 \text{ MPa}$  and  $U(\eta) = 4\%$  ( $k=2$ ).

**TABLE 4**

Parameters and relative deviations for VFT model, equation (6).

Parameters	Values
$a_1 \cdot 10^3 / \text{MPa}^{-1}$	1.04106
$a_2 \cdot 10^6 / \text{MPa}^{-2}$	-2.31600
$b_1 / \text{MPa}^{-1} \cdot \text{K}$	2.81118
$b_2 \cdot 10^3 / \text{MPa}^{-2} \cdot \text{K}$	-3.16018
$b_3 \cdot 10^6 / \text{MPa}^{-3} \cdot \text{K}$	3.29849
AAD / %	1.5
Bias / %	-0.15
MD / %	8.9

**TABLE 5**

Deviations obtained for the different datasets with the modified VFT equation (6).

	AAD	MD	Bias
FB-UPPA	1.3	5.0	0.6
QCR-UPPA 1	1.3	8.0	-0.3
QCR-UPPA 2	1.3	7.1	0.0
FB-USC VisLPT1	3.1	8.9	-0.4
FB-USC VisLPT2	1.8	7.1	0.2
FB-UNSW	1.2	4.1	-0.9

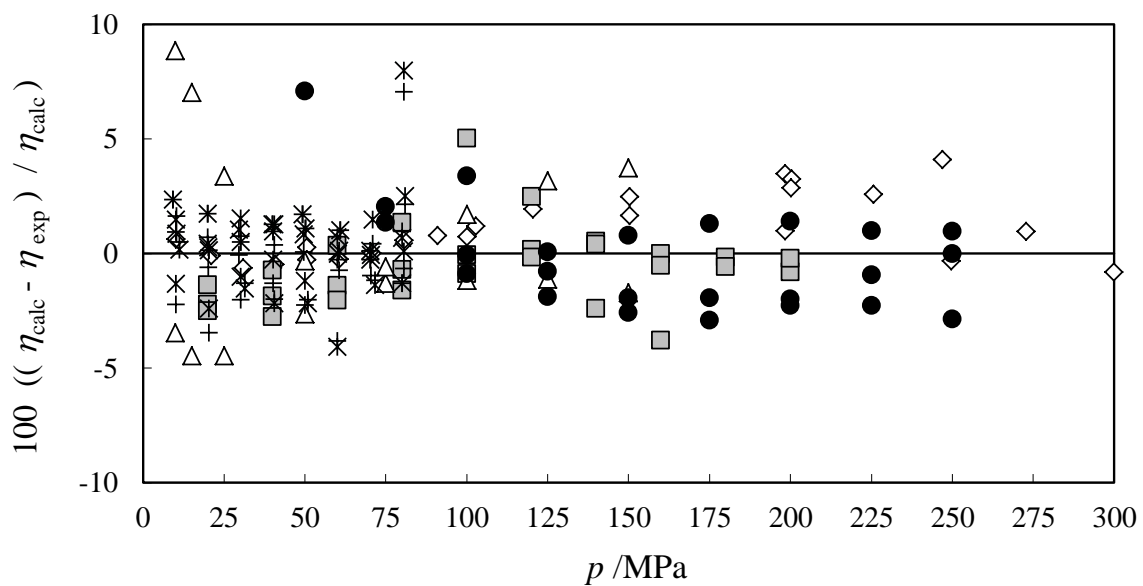
**TABLE 6**Parameters  $a_0$ ,  $a_1$ ,  $a_2$ ,  $a_3$  and  $\gamma$  for thermodynamic scaling, equation (11).

Parameters	Values
$a_0$	-15.7798
$10^3 \cdot a_1$	-0.262343
$10^5 \cdot a_2$	1.52152
$10^9 \cdot a_3$	-1.37933
$\gamma$	4.14795
AAD / %	1.5
Bias / %	-0.11
MD / %	9.3

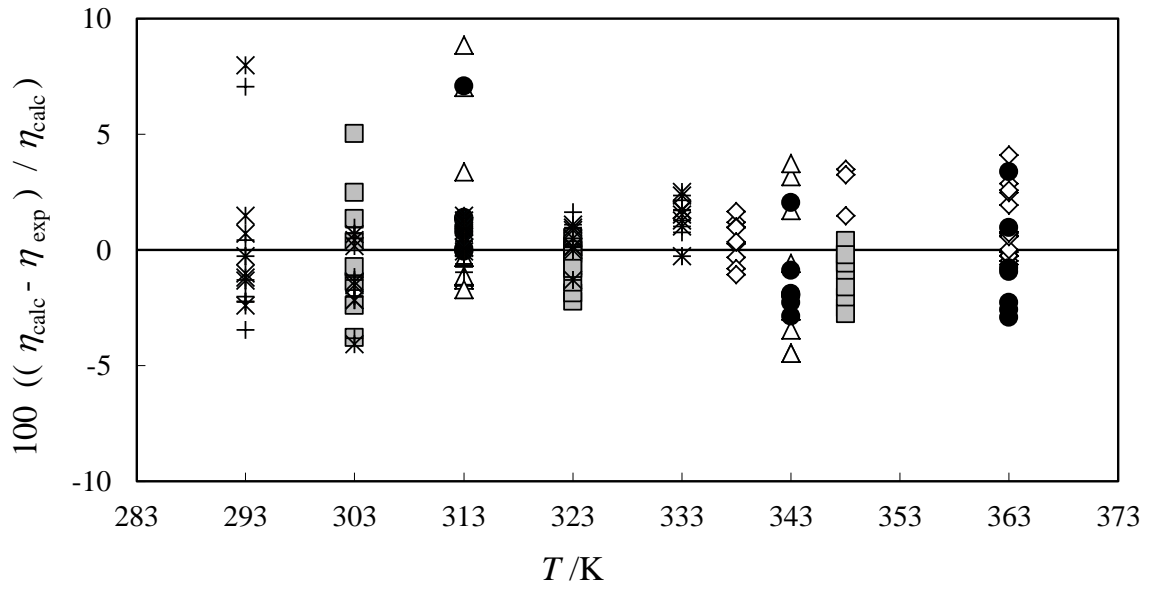
**TABLE 7**

Deviations obtained for the different datasets with equation (11).

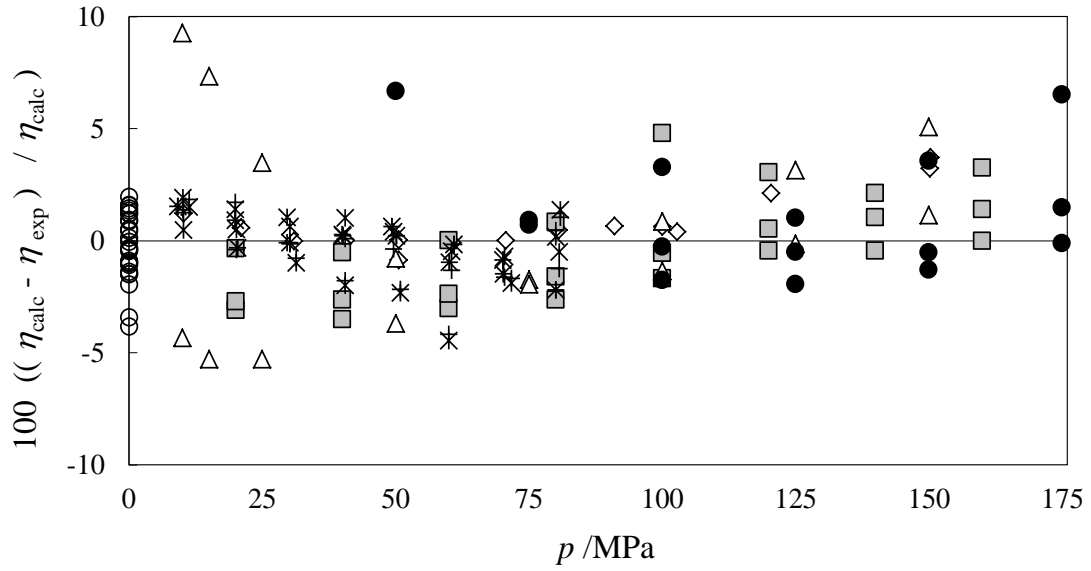
	AAD	MD	Bias
FB-UPPA	1.8	4.8	0.4
QCR-UPPA 1	1.2	4.5	-0.1
QCR-UPPA 2	1.0	4.2	0.3
FB-USC VisLPT1	3.4	9.3	-0.4
FB-USC VisLPT2	2.0	6.7	-1.2
FB-UNSW	1.0	3.7	-0.9



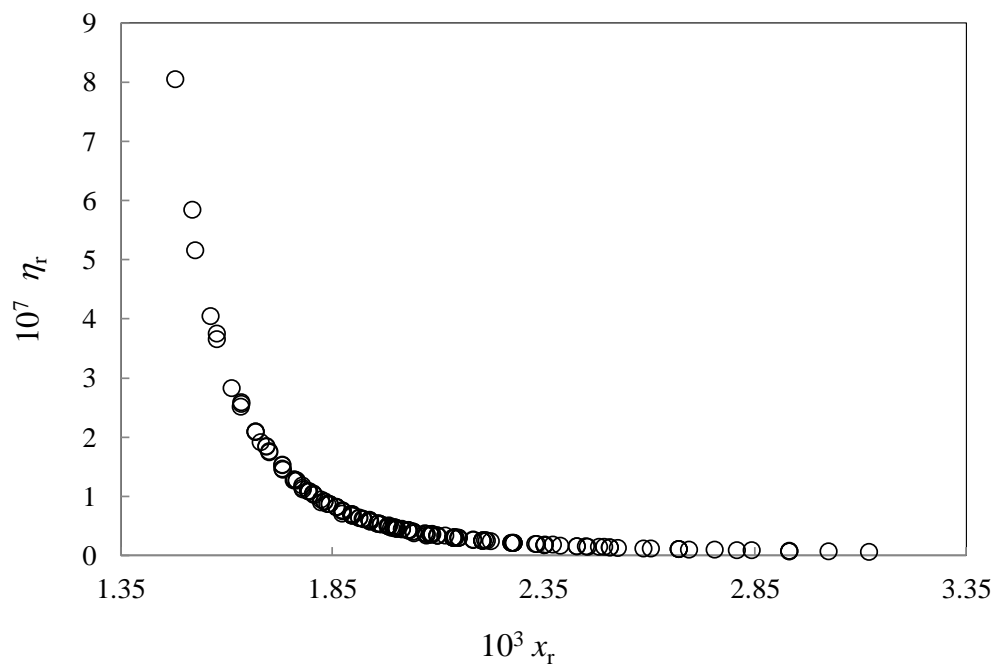
**Figure 1.** Percentage deviations of the viscosity data, given as a function of the pressure, from the values calculated from equation (6) (VFT model). FB-UNSW ( $\diamond$ ), FB-UPPA ( $\blacksquare$ ), FB-USCVisLPT1 ( $\triangle$ ), FB-USCVisLPT2 ( $\bullet$ ), QCR-UPPA 1 ( $*$ ) and QCR-UPPA 2 ( $+$ ).



**Figure 2.** Percentage deviations of the viscosity data, given as a function of the temperature, from the values calculated from equation (6) (VFT model). FB-UNSW ( $\diamond$ ), FB-UPPA ( $\blacksquare$ ), FB-USCVisLPT1 ( $\triangle$ ), FB-USCVisLPT2 ( $\bullet$ ), QCR-UPPA 1 ( $*$ ) and QCR-UPPA 2 ( $+$ ).



**Figure 3.** Percentage deviations of the viscosity data, given as a function of the pressure, from the values calculated with equation (11) (Thermodynamic scaling model). FB-UNSW ( $\diamond$ ), FB-UPPA ( $\blacksquare$ ), FB-USCVisLPT1 ( $\triangle$ ), FB-USCVisLPT2 ( $\bullet$ ), QCR-UPPA 1 ( $*$ ), QCR-UPPA 2 ( $+$ ) and [12] ( $\circ$ ).



**Figure 4.** Experimental reduced viscosity  $\eta_r$  versus  $x_r = T_r / \rho_r^\gamma$  ( $303.15 < T/K < 363.15$ ,  $p < 176$  MPa and  $\gamma = 4.15$ )