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Compressed Liquid Densities of Squalane and Pentaerythritol Tetra(2-ethylhexanoate)†

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New experimental densities are reported for squalane and for branched pentaerythritol tetra(2-ethylhexanoate), PEB8, in the compressed liquid state over the temperature range from (278.15 to 353.15) K and for pressures up to 45 MPa. The reliability of the technique and the procedure up to 25 MPa has been verified in our previous works, and in the present work they were checked up to 45 MPa by comparing our experimental densities for heptane with literature data. A total of 297 density values have been measured with a high-pressure vibrating tube densimeter. The correction factor for density due to the sample viscosity has been considered. This factor ranges from 1×10^{-4} to 1×10^{-3} g·cm^{-3} for PEB8 and from 4×10^{-5} to 6×10^{-4} g·cm^{-3} for squalane over the entire *Tp* interval. The pressure and temperature dependencies of squalane and PEB8 densities could be accurately represented by the Tammann−Tait equation with standard deviations of 3×10^{-5} g·cm^{-3} for squalane and 9×10^{-5} g·cm^{-3} for PEB8. These density data were used to analyze the isothermal compressibility, the isobaric thermal expansivity, and the internal pressure of squalane and PEB8.

Introduction

Polyol esters (POEs) have being used as lubricants for commercial applications because of their characteristic properties and their environmentally safe usage.[1] POEs lubricants have favorable properties as refrigeration oils compared to those of polyalkylene glycols. They are less hygroscopic, have higher miscibilities with HFCs and CO_2 refrigerants, and are miscible with mineral oils.[2,3] Lubricants based on polyol esters represent one of the most important types of synthetic lubricants.[4,5] Their high thermal stability and good lubricating properties have resulted in a wide range of applications from the textile industry to gas turbine motors.[6] To minimize costly experimentation, new models that can predict the thermodynamic and transport properties of POEs would be very useful,[7] but for this purpose a more complete database of thermophysical properties over wide temperature and pressure ranges is needed.

One of the goals of our present project is to provide the thermophysical properties over wide temperature and pressure ranges for one type of POE with known structure, namely, pentaerythritol tetraalkyl esters (PEs),[7,8] which consist of an isopentane nucleus linked to four identical alkyl ester chains (branched or linear). With this aim, in the present work the volumetric properties of pentaerythritol tetra(2-ethylhexanoate), PEB8, have been studied. To our knowledge, only Wahlström and Vamling[7] have reported density measurements for PEB8 over the temperature interval of (299.26 to 352.92) K and only at atmospheric pressure. Shobha and Kishore[9] have published the densities at 0.1 MPa from (303 to 413) K for pentaerythritol tetraoctanoate, which is isomeric with PEB8.

The volumetric behavior of squalane at high pressures is also studied in this work. This fluid can be considered to be a model substance for mineral lubricating oils because of its characteristic thermophysical properties. It is used mainly as a base oil for mechanical and electrical contacts and in pharmaceutical and cosmetic applications. To determine the viscosity of POEs, squalane is a useful fluid to verify the viscometer calibration at high viscosities, and for this purpose the density of this fluid is needed. At atmospheric pressure, Fermeglia and Torriano[10] have reported the density of squalane at 298.15 K, and Kuss and Taslimi,[11] from (298.15 to 353.15) K. At high pressures, the data are very scarce—only four experimental points are reported by Kuss and Taslimi[11] at 39.223 MPa over the temperature range from (298.15 to 353.15) K.

In the present work, new experimental densities are reported for branched PEB8 and squalane in the compressed liquid phase between (278.15 and 353.15) K and at pressures up to 45 MPa. The densities of heptane have also been measured and compared with several literature sources to verify the calibration procedure up to 45 MPa. The experimental density data were used to determine isothermal compressibilities, κ_T, and isobaric thermal expansivities, α_p, for branched PEB8 and squalane. These values can be used for the evaluation of predictive thermodynamic models such as equations of state.

Experimental Section

Materials. Squalane (2,6,10,15,19,23-Hexamethyltetracosane, CAS 111-01-3, $C_{30}H_{62}$) and heptane were obtained from Aldrich (puriss 99%) and from Fluka (puriss ≥99.5%), respectively. Pentaerythritol tetra(2-ethylhexanoate) (PEB8, CAS 7299-99-2, $C_{37}H_{68}O_8$) was obtained from Nikkol Chemicals (puriss 99%). These chemicals, as well as water (purified using a Milli-Q Plus system, with a resistivity of 18.2 MΩ·cm at 298.15 K), were partially degassed before use with a Branson 2210 ultrasonic bath. The molecular structures of squalane and branched pentaerythritol tetra(2-ethylhexanoate) are presented in Figure 1.

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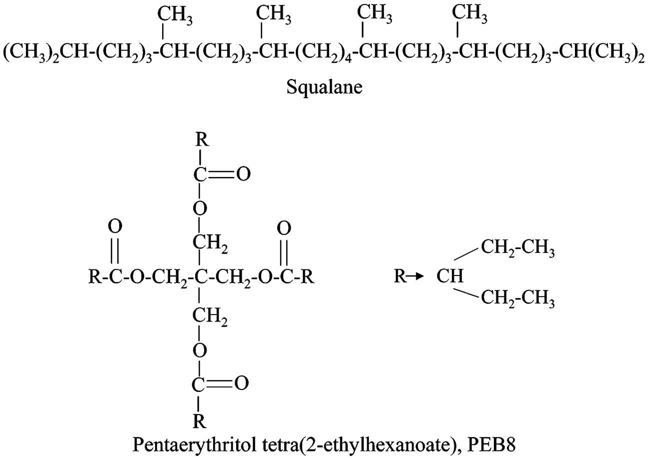

Figure 1. Molecular structures of squalane and PEB8.

Experimental Method. The density was measured as a function of pressure and temperature using a vibrating tube densimeter technique, and the heart of the equipment is a commercial Anton Paar DMA 512P vibrating cell. The complete experimental assembly of the apparatus and the experimental procedure have been previously described in detail.[12,13] The temperature was regulated by circulating water from an external temperature-controlled circulating bath (Polyscience PS 9110) through the heat exchanger of the vibrating tube cell. The temperature inside the cell block was measured with an Anton Paar CKT100 platinum resistance thermometer with an uncertainty of ±0.01 K. The temperature scale employed was ITS-90. The pressure was measured by means of an HBM-PE300 differential pressure gauge. This manometer was calibrated with an uncertainty of ±0.02 MPa.

Among the diverse ways[14] to convert the vibrating periods to densities, in this work the method developed by Lagourette et al.[15] was used. To apply this method, it is necessary to know only the vibrating period of the evacuated tube over the entire experimental temperature range and the vibrating period of a reference fluid as a function of temperature and pressure. A classical reference fluid is water, for which precise density data are available as a function of T and p.[16]

There are systematic errors in the densities measured with vibrating tube densimeters due to the sample viscosity. Bernhart and Pauly[17] have compared at atmospheric pressure the density measurements carried out with a pycnometer and with a DMA 02C densimeter (Anton Paar) for several mixtures, such as water + glycerol. They have found that for viscosities higher than (1 or 2) mPa·s the density data obtained with the DMA 02C densimeter exceeded the pycnometer values by a substantial amount, for example, 1×10^{-4} g·cm^{-3} for a sample of viscosity of 10 mPa·s. Subsequently, Ashcroft et al.[18] have fitted the relative density increase in terms of the sample viscosity for a DMA 602 densimeter, also using water + glycerol data, but only at atmospheric pressure. The correction factor found by Ashcroft et al. (DMA 602) was significant different than those found by Bernhart and Pauly (DMA 02C), so the systematic error depends not only on the sample viscosity but also on the specific design of the oscillator tube.[17,18]

Following the available commercial information from Anton Paar on its vibrating tube densimeters, the density correction for a DMA 512 and for samples with viscosity values higher than 15 mPa·s would be around 5.5×10^{-5} g·cm^{-3}, which is lower than the experimental uncertainty obtained by several authors.[19-22] For this reason in the most of the cases the density correction factor for the DMA 512 densimeter was not considered even in some studies[22] concerning binary and ternary polymer solutions with high viscosity values (poly(ethylene glycol) PEG-200 and poly(propylene glycol) PPG-425, whose viscosities at 298.15 K and 0.1 MPa are around 50 mPa·s and 70 mPa·s, respectively). Taking into account that the dynamic viscosity of PEB8 and squalane at 303.15 K and 0.1 MPa is around 60 mPa·s and 20 mPa·s,[23] respectively, a correction to the density measurements could be necessary. In the present work, the following equation recently recommended by Anton Paar[24] for the DMA 512 densimeter has been used to calculate the correction factor $\Delta\rho$

$$\frac{\Delta\rho}{\rho} = [-0.5 + 0.45\sqrt{\eta}]10^{-4} \qquad (1)$$

where ρ represents the density value obtained from the densimeter calibration and the measured periods, $\Delta\rho$ is the difference between this ρ value and the "corrected" density value due to the effect of viscosity, and η is the dynamic viscosity of the sample in mPa·s. The viscosity values of PEB8 and squalane have been taken from Pensado et al.[23] In the case of PEB8, the correction factor, $\Delta\rho$, ranges from 1×10^{-4} to 1×10^{-3} g·cm^{-3} and for squalane from 4×10^{-5} to 6×10^{-4} g·cm^{-3}. The total estimated density uncertainty without viscosity correction but taking into account the uncertainty of the temperature, the pressure, the period of oscillation measurements for water, vacuum, and the studied liquids (seven-digit frequency counter), and the water density accuracy is 1×10^{-4} g·cm^{-3}.

Results and Discussion

Densities. The density measurements of heptane, squalane, and PEB8 reported in Table 1 were performed along 9 isotherms between (278.15 and 353.15) K and along 11 isobars at pressures up to 45 MPa. In the case of PEB8 and squalane, it was necessary to introduce the correction factor due to the viscosity; for this purpose, eq 1 has been utilized together with the viscosity values previously reported by Pensado et al.[23] The density behavior is standard: ρ increases when the temperature decreases or the pressure increases. The density data of squalane are lower than those of PEB8. The experimental $p\rho T$ values for heptane, squalane, and PEB8 were fitted with the following modified Tammann−Tait equation

$$\rho(T, p, C, B) = \frac{\rho(T, 0.1\ \mathrm{MPa})}{1 - C \ln\left(\dfrac{B(T) + p}{B(T) + p_{\mathrm{ref}}(T)}\right)} \qquad (2)$$

where $\rho(T, 0.1\ \mathrm{MPa})$ is the temperature dependence of the density at atmospheric pressure that is given by

$$\rho(T, 0.1\ \mathrm{MPa}) = \sum_{i=0}^{N} A_i T^i \qquad (3)$$

The A_i values were determined by smoothing the experimental densities at atmospheric pressure with standard deviations, σ^*, of 10×10^{-5}, 5×10^{-5}, and 10×10^{-5} g·cm^{-3} for heptane, squalane, and PEB8, respectively. The denominator of eq 2 changes with both temperature and pressure. The parameter C was assumed to be temperature-independent, and for $B(T)$, the follow

Table 1. Experimental Densities[a] at Different Temperatures *T* and Pressures *p*

	T/K								
p/MPa	278.15	283.15	293.15	303.15	313.15	323.15	333.15	343.15	353.15
					ρ/g·cm^{-3}				
					Heptane				
0.1	0.69636	0.69223	0.68379	0.67535	0.66686	0.65790	0.64877	0.63969	0.63049
1	0.69701	0.69301	0.68460	0.67616	0.66770	0.65885	0.64992	0.64093	0.63183
5	0.70047	0.69639	0.68822	0.68006	0.67191	0.66324	0.65480	0.64623	0.63760
10	0.70435	0.70044	0.69249	0.68463	0.67680	0.66853	0.66046	0.65233	0.64413
15	0.70803	0.70424	0.69652	0.68892	0.68135	0.67344	0.66566	0.65790	0.65011
20	0.71154	0.70785	0.70034	0.69296	0.68563	0.67794	0.67049	0.66304	0.65553
25	0.71488	0.71127	0.70398	0.69680	0.68969	0.68225	0.67503	0.66786	0.66064
30	0.71817	0.71456	0.70762	0.70052	0.69353	0.68630	0.67930	0.67237	0.66538
35	0.72123	0.71781	0.71090	0.70400	0.69719	0.69015	0.68335	0.67661	0.66983
40	0.72419	0.72080	0.71410	0.70730	0.70067	0.69383	0.68719	0.68063	0.67408
45	0.72705	0.72372	0.71714	0.71051	0.70402	0.69733	0.69085	0.68447	0.67804
					Squalane				
0.1	0.81810 (0.81841)	0.81475 (0.81501)	0.80827 (0.80845)	0.80188 (0.80201)	0.79553 (0.79563)	0.78906 (0.78914)	0.78273 (0.78279)	0.77631 (0.77636)	0.77003 (0.77006)
1	0.81859 (0.81890)	0.81525 (0.81551)	0.80881 (0.80899)	0.80243 (0.80256)	0.79612 (0.79622)	0.78969 (0.78976)	0.78337 (0.78343)	0.77700 (0.77705)	0.77073 (0.77076)
5	0.82071 (0.82104)	0.81745 (0.81772)	0.81110 (0.81129)	0.80487 (0.80501)	0.79864 (0.79875)	0.79234 (0.79243)	0.78619 (0.78625)	0.77993 (0.77998)	0.77384 (0.77388)
10	0.82331 (0.82367)	0.82016 (0.82045)	0.81388 (0.81409)	0.80778 (0.80793)	0.80168 (0.80179)	0.79554 (0.79563)	0.78956 (0.78962)	0.78345 (0.78351)	0.77750 (0.77755)
15	0.82581 (0.82620)	0.82272 (0.82304)	0.81658 (0.81680)	0.81059 (0.81075)	0.80461 (0.80473)	0.79863 (0.79872)	0.79276 (0.79283)	0.78681 (0.78687)	0.78102 (0.78107)
20	0.82824 (0.82866)	0.82521 (0.82555)	0.81918 (0.81942)	0.81329 (0.81346)	0.80743 (0.80756)	0.80158 (0.80168)	0.79583 (0.79591)	0.79003 (0.79009)	0.78436 (0.78441)
25	0.83059 (0.83103)	0.82762 (0.82798)	0.82167 (0.82193)	0.81592 (0.81610)	0.810216 (0.81030)	0.80445 (0.80456)	0.79879 (0.79887)	0.79312 (0.79319)	0.78757 (0.78762)
30	0.83287 (0.83334)	0.82994 (0.83033)	0.82414 (0.82441)	0.81845 (0.81865)	0.81278 (0.81293)	0.80717 (0.80729)	0.80162 (0.80171)	0.79608 (0.79615)	0.79066 (0.79072)
35	0.83507 (0.83559)	0.83223 (0.83265)	0.82649 (0.82678)	0.82092 (0.82113)	0.81535 (0.81551)	0.80984 (0.80996)	0.80439 (0.80449)	0.79894 (0.79902)	0.79362 (0.79368)
40	0.83721 (0.83776)	0.83441 (0.83485)	0.82881 (0.82912)	0.82329 (0.82351)	0.81781 (0.81798)	0.81242 (0.81255)	0.80703 (0.80713)	0.80171 (0.80179)	0.79647 (0.79654)
45	0.83931 (0.83990)	0.83654 (0.83702)	0.83104 (0.83137)	0.82561 (0.82585)	0.82022 (0.82040)	0.81491 (0.81505)	0.80962 (0.80973)	0.80440 (0.80448)	0.79924 (0.79931)
					Pentaerythritol Tetra(2-ethylhexanoate) (PEB8)				
0.1	0.97186 (0.97276)	0.96845 (0.96915)	0.96162 (0.96207)	0.95472 (0.95503)	0.947876 (0.94798)	0.94045 (0.94062)	0.93358 (0.93371)	0.92649 (0.92659)	0.91945 (0.91953)
1	0.97235 (0.97326)	0.96897 (0.96967)	0.96216 (0.96261)	0.95527 (0.95558)	0.94835 (0.94857)	0.94125 (0.94141)	0.93421 (0.93434)	0.92717 (0.92727)	0.92014 (0.92022)
5	0.97457 (0.97552)	0.97124 (0.97198)	0.96455 (0.96502)	0.95779 (0.95812)	0.95098 (0.95121)	0.94386 (0.94404)	0.93713 (0.93727)	0.93023 (0.93034)	0.92334 (0.92342)
10	0.97726 (0.97826)	0.97405 (0.97483)	0.96746 (0.96797)	0.96083 (0.96118)	0.95414 (0.95439)	0.94720 (0.94740)	0.94066 (0.94081)	0.93389 (0.93401)	0.927129 (0.92728)
15	0.97987 (0.98092)	0.97674 (0.97756)	0.97030 (0.97083)	0.96379 (0.96416)	0.95723 (0.95750)	0.95044 (0.95065)	0.94402 (0.94418)	0.93742 (0.93754)	0.93084 (0.93094)
20	0.98242 (0.98352)	0.97935 (0.98021)	0.97300 (0.97359)	0.96665 (0.96704)	0.96021 (0.96049)	0.95354 (0.95376)	0.94727 (0.94744)	0.94081 (0.94094)	0.93437 (0.93447)
25	0.98485 (0.98601)	0.98187 (0.98278)	0.97567 (0.97626)	0.96941 (0.96983)	0.96310 (0.96340)	0.95657 (0.95680)	0.95040 (0.95058)	0.94409 (0.94423)	0.93777 (0.93788)
30	0.98727 (0.98848)	0.98434 (0.98529)	0.97827 (0.97889)	0.97211 (0.97255)	0.96589 (0.96622)	0.95948 (0.95973)	0.95341 (0.95360)	0.94723 (0.94737)	0.94105 (0.94117)
35	0.98960 (0.99088)	0.98675 (0.98775)	0.98077 (0.98143)	0.97473 (0.97519)	0.96862 (0.96896)	0.96232 (0.96257)	0.95637 (0.95657)	0.95027 (0.95042)	0.94419 (0.94431)
40	0.99189 (0.99322)	0.98906 (0.99011)	0.98323 (0.98392)	0.97727 (0.97776)	0.97126 (0.97162)	0.9650 (0.96534)	0.95921 (0.95942)	0.95323 0.95340)	0.94727 (0.94740)
45	0.99412 (0.99552)	0.99135 (0.99245)	0.98561 (0.98633)	0.97976 (0.98027)	0.97382 (0.97420)	0.96775 (0.96803)	0.96198 (0.96220)	0.95609 (0.95626)	0.95024 (0.95037)

[a] The values in parentheses are the direct experimental measurements without consideration of the correction factor due to the sample viscosity.

ing polynomial function was used:

$$B(T) = \sum_{i=0}^{N} B_i T^i \tag{4}$$

The values of B_i and C for each compound have been determined by least-squares (using Marquardt's algorithm) fitting eq 2 to all of the experimental data at pressures different than atmospheric. The set of coefficient values (A_i, B_i, C) obtained are listed in Table 2. The standard deviations σ (also reported in Table 2) are lower or equal to the experimental uncertainty (1×10^{-4} g·cm^{-3}). The number of parameters has been determined using an F-test. The relative deviations between the experimental data and those calculated with the Tammann−Tait equation (eq 2) are presented in Figure 2 for heptane, squalane, and branched PEB8.

Table 2. A_i, B_i, and C Coefficients and Standard Deviations, σ^* and σ, Obtained from the Tammann−Tait Density Correlation against Both the Temperature and the Pressure (Equation 2)

parameters	heptane	squalane	PEB8
A_0/g·cm^{-3}	0.86217	1.00727	1.14883
10^4A_1/g·cm^{-3}K^{-1}	−3.736	−7.119	−5.855
10^7A_2/g·cm^{-3}K^{-2}	−8.001	1.1338	−1.8180
σ^*/g·cm^{-3}	10×10^{-5}	5×10^{-5}	1×10^{-4}
C	0.08559	0.07917	0.07993
B_0/MPa	304.06	434.99	517.95
B_1/MPa·K^{-1}	−1.1299	−1.5896	−1.9371
10^3B_2/MPa·K^{-2}	1.0449	1.6265	2.0517
σ/g·cm^{-3}	6×10^{-5}	3×10^{-5}	9×10^{-5}

In previous works, the calibration procedure was carried out up to 25 MPa; in this paper, new densimeter calibration parameters for a larger pressure range (up to 45 MPa) have been determined. To verify the new calibration range, we have compared our experimental values for heptane with $p\rho$T literature data reported by several authors.[20,25−27] The experimental density measurements of heptane reported in Table 1 present an average absolute deviation (AAD) of 0.02% with the reference data calculated from the Tammann−Tait correlation proposed by Cibulka and Hnědkovský,[26] the maximum deviation being 0.07% at 0.1 MPa and 353.15 K. The AAD and the maximum deviations with the correlation proposed by Assael et al.,[25] which covers densities of alkanes (from ethane to hexadecane), are 0.05% and 0.09%, respectively. Our density values of heptane also agree with those recently reported by Pecar and Dolecek[20] within an average deviation of 0.04% and a maximum deviation of 0.11% (at 348.15 K and 40 MPa). Figure 3a shows the relative percentage deviations between our experimental data and those $p\rho$T literature values against the pressure up to 45 MPa.

For squalane, in addition to the data at atmospheric pressure and 298.15 K reported by Fermeglia and Torriano,[10] there are eight values at (0.0981 and 39.223) MPa and (298.15, 313.15, 333.15, and 353.15) K due to Kuss and Taslimi.[11] Taking into account that the density data reported in this work (Table 1) are not at the same temperature or pressure as the literature data of squalane, we have used interpolated densities from eq 2 for comparison. The relative deviation between our interpolated value and the data of Fermeglia and Torriano[10] is 0.005%. The average absolute deviation with the data of Kuss and Taslimi[11] is 0.04%, the maximum deviation being 0.07% at 333.15 K. The purity of the squalane samples used by Fermeglia and Torriano[10] and in the present work are the same, 99%, whereas the purity of that used by Kuss and Taslimi[11] is not given in their article. Figure 3b shows the relative percentage deviations between our experimental data of squalane and those in the literature.[10,11]

For PEB8, our experimental data have been compared with those reported by Wahlström and Vamling[7] at 0.1 MPa over the temperature interval from (299.26 to 352.92) K, obtaining an AAD of 0.3% with the maximum deviation being 0.5% at 352.92 K. These authors[7] have made density measurements with a DMA 602 tube densimeter with an estimated uncertainty of 0.1%, and they have not considered the viscosity correction factor. Furthermore, it is necessary to take into account that the sample of PEB8 used by Wahlström and Vamling has been synthesized by the authors, obtaining an estimated purity of >90%, whereas the sample used in this work has a purity of 99%.

Isothermal Compressibility. The temperature and pressure dependence of the isothermal compressibility was calculated according to its definition, $\kappa_T = (1/\rho)(\partial\rho/\partial p)_T$, from the analytical differentiation of the Tammann−Tait equation with respect to pressure. This method is certainly the most direct way to obtain reliable isothermal compressibility values[28] from density measurements. From eq 2, the following expression is obtained:

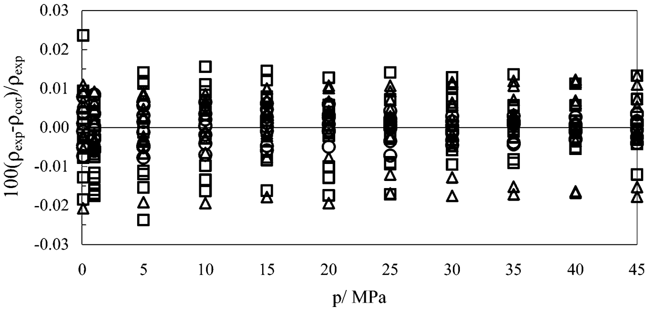

Figure 2. Relative deviations between the experimental data and those calculated with the Tammann−Tait equation (eq 2) for □, heptane; ○, squalane; and △, PEB8.

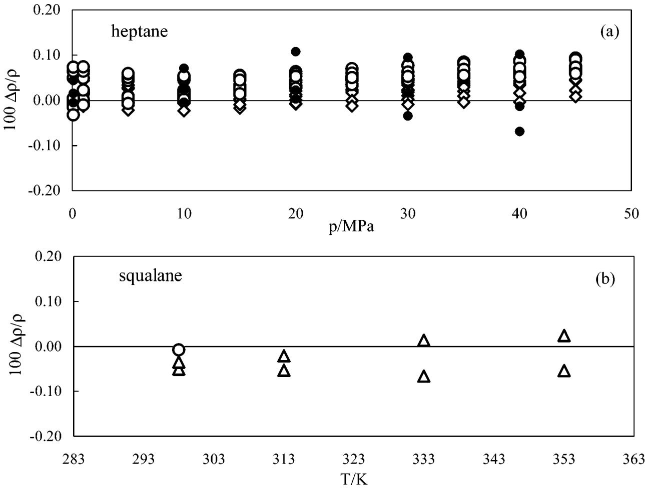

Figure 3. Relative deviations between the experimental density data of this work and those reported by other authors: (a) ○, Assael et al.;[25] △, Cibulka and Hnedkovský;[26] ●, Pecar and Dolecek.[20] (b) ○, Fermeglia and Torriano;[10] △, Kuss and Taslimi.[11]

$$\kappa_T(T, p) = \frac{C}{(B(T) + p)\left[1 - C \ln\dfrac{B(T) + p}{B(T) + 0.1\ \text{MPa}}\right]} \qquad (5)$$

The values of the C parameter and of B_i coefficients for the temperature function $B(T)$ are taken from Table 2 for squalane and PEB8.

The isothermal compressibility values obtained with eq 5 were verified from those estimated by correlating the density, over each isotherm $\rho(p)$, using eq 2 keeping B and C as constant values for each temperature and using in the numerator on the right side of eq 2 the density value at 0.1 MPa. The B and C parameters and the standard deviation, σ, obtained for each isotherm are reported in Table 3. In this case, a total of 18 parameters are needed for each compound over the full temperature experimental range instead of 7 and 6 parameters (for squalane and PEB8, respectively) that were used to correlate density against both temperature and pressure. As can be seen in Table 3, the standard deviations, σ, of the $\rho(p)$ correlations at fixed temperature are 1×10^{-5}g·cm^{-3} for squalane and $\leq 5 \times 10^{-5}$g·cm^{-3} for PEB8.

Table 3. *B* and *C* Coefficients and Standard Deviations, *σ*, Obtained by Correlating, at Each Constant Temperature, the Density against Pressure, *ρ*(*p*)

	squalane			PEB8		
T/K	B/MPa	C	σ/g·cm^{-3}	B/MPa	C	σ/g·cm^{-3}
278.15	0.07651	114.65	1×10^{-5}	0.07729	133.55	1×10^{-5}
283.15	0.07500	108.04	1×10^{-5}	0.07491	124.25	1×10^{-5}
293.15	0.08057	110.75	1×10^{-5}	0.07917	124.67	1×10^{-5}
303.15	0.07908	102.35	1×10^{-5}	0.08088	120.71	1×10^{-5}
313.15	0.08063	99.14	1×10^{-5}	0.08160	115.53	1×10^{-5}
323.15	0.08024	92.51	1×10^{-5}	0.07956	105.46	5×10^{-5}
333.15	0.07822	84.83	1×10^{-5}	0.07973	100.10	2×10^{-5}
343.15	0.08005	82.06	1×10^{-5}	0.07967	94.44	1×10^{-5}
353.15	0.07969	77.08	1×10^{-5}	0.08157	91.99	2×10^{-5}

Table 4. Isobaric Thermal Expansivity and Isothermal Compressibility for Squalane and PEB8

	$10^4\alpha_p$/K^{-1}			$10^4\kappa_T$/ MPa^{-1}		
p/MPa	293.15	323.15	343.15	293.15	323.15	343.15
			Squalane			
1	7.94	8.05	8.12	7.22	8.60	9.66
10	7.59	7.63	7.66	6.71	7.89	8.78
20	7.26	7.24	7.24	6.23	7.23	7.97
30	6.97	6.91	6.89	5.81	6.68	7.31
			Pentaerythritol Tetra(2-ethylhexanoate) (PEB8)			
1	7.16	7.43	7.62	6.27	7.51	8.34
10	6.85	7.08	7.24	5.89	6.97	7.68
20	6.56	6.74	6.88	5.52	6.45	7.06
30	6.29	6.44	6.57	5.19	6.02	6.54

There is excellent agreement between the isothermal compressibilities calculated from the global correlation, $\rho(T, p)$, and those obtained with the individual correlations at each temperature, $\rho(p)$. Thus, the AAD and bias between both data series are 0.2% and −0.01% for squalane and 0.4% and −0.03% for PEB8, respectively. The maximum deviations are reached at 283.15 K and 1 MPa (1.1% for squalane and 1.5% for PEB8). The isothermal compressibility values for squalane and PEB8 obtained with the global correlation are reported in Table 4 at some temperatures and pressures. The uncertainty of κ_T is estimated to be $\pm 0.06 \times 10^{-4}$ MPa^{1-} (±1%) over the entire pressure and temperature ranges. Troncoso et al.[29] and Piñeiro et al.[30,31] used the same procedure to determine κ_T for pure *n*-perfluoroalkanes,[30] hydrofluoroethers,[31] and 1-hexanol + hexane mixtures[29] with an estimated uncertainty of $\pm 0.4 \times 10^{-4}$ MPa^{-1}. Several authors[32–34] also estimate the isothermal compressibility from volumetric measurements but using a correlation of the volume ratios with the secant bulk modulus equation. The uncertainty estimated by Back et al.[32] with this method for κ_T is between 1% and 2%. We have also calculated the isothermal compressibility using the secant bulk modulus equation and have found an average deviation of 0.3% with the values estimated with eq 2 for both squalane and PEB8. The maximum deviations are 0.9% for squalane and 1.3% for PEB8. The advantage of using eq 2 instead of the secant bulk modulus is that eq 2 is more accurate for density extrapolation in pressure beyond the range of the experimental data.[32] In Figure 4a and b, the isothermal compressibilities of squalane and PEB8 are plotted against pressure at different temperatures. The values of this derived property are a little higher for squalane than for PEB8, so squalane is slightly more compressible than PEB8.

Isobaric Thermal Expansivity. In a similar way as for κ_T and according to its definition $\alpha_p = -(1/\rho)(\partial\rho/\partial T)_p$, the isobaric thermal expansivity data can be determined by analytical differentiation of eq 2 with respect to temperature. Considering eqs 3 and 4 for the temperature dependencies of $\rho(T, 0.1\ \text{MPa})$ and of $B(T)$, we can express this derived property as follows

$$\alpha_p(T, p) = -\frac{A_1 + 2A_2T}{\rho(T, 0.1\ \text{MPa})} - \frac{C(0.1\ \text{MPa} - p)}{(B(T) + p)(B(T) + 0.1\ \text{MPa})}\,\frac{B_1 + 2B_2T}{\left[1 - C\ln\left(\dfrac{B(T) + p}{B(T) + 0.1\ \text{MPa}}\right)\right]} \tag{6}$$

where the density is expressed in g·cm^{-3}, the pressure, in MPa, and the temperature, in K. The values of parameters C, A_1, A_2, B_1, and B_2 are taken from Table 2 for squalane and PEB8.

In the present work, another way to calculate the isobaric thermal expansivity has been considered, and over each isobar, the density was correlated with the temperature using a simple polynomial function (similar to eq 3). The polynomial correlation $\rho(T)$ is performed at fixed pressure, and then the derivative with respect to temperature, $(\partial\rho/\partial T)_p$, is determined. In this case, a total of 33 parameters are needed for each compound over the full temperature and pressure experimental ranges. The standard deviations, σ, of the $\rho(T)$ correlations at fixed pressure are always $\leq 5 \times 10^{-5}$g·cm^{-3} and 1×10^{-4}g·cm^{-3} for squalane and PEB8, respectively. The comparison among the α_p values calculated from the global correlation, eq 6, with those obtained with the individual correlations at each fixed pressure, $\rho(T)$, gives average absolute deviations of 0.1% and 0.5% for squalane and PEB8, respectively. The maximum deviations are 0.5% for squalane (at 343.15 K and 15 MPa) and 1.7% for PEB8 (at 343.15 K and 0.1 MPa). The α_p values for squalane and PEB8 obtained with the global correlation are reported in Table 4 at some temperatures and pressures. The uncertainty of α_p is estimated to be $\pm 0.3 \times 10^{-4}$ K^{-1} (±4%) over the entire pressure and temperature ranges.

Troncoso et al.[29] and Piñeiro et al.[30] consider two different procedures to determine α_p from density measurements; the first one is similar to those used in the present work—analytical differentiation of the global correlation $\rho(p,T)$—and the second one, as named by the authors, is the incremental procedure,[35] which briefly consists of the evaluation of the density change, $\Delta\rho$, corresponding to a temperature change, ΔT. This temperature interval, ΔT, is chosen by these authors by taking into account that the density should vary linearly. These authors[29,30] found deviations between both methods that were systematically smaller than their estimated uncertainties of $\pm 0.3 \times 10^{-4}$ K^{-1} and $\pm 3 \times 10^{-4}$ K^{-1}. We have also utilized the incremental procedure, comparing the α_p results obtained with this method with those obtained from eq 6. The AADs and maximum deviations between both data series are, respectively, $\pm 0.002 \times 10^{-4}$ K^{-1} and $\pm 0.003 \times 10^{-4}$ K^{-1} for squalane and $\pm 0.003 \times 10^{-4}$ K^{-1} and 0.005×10^{-4} K^{-1} for PEB8. These deviations are clearly lower than the estimated uncertainty.

In Figure 4c and d, the isobaric thermal expansivities of squalane and PEB8 are plotted against pressure at different temperatures. Squalane is slightly more expandable and compressible than PEB8 under the same *Tp* conditions, probably because of a larger free volume in the case of squalane. As can also be shown in these Figures, the α_p isotherms for squalane have an intersection point, whereas for PEB8 this point is beyond the studied pressure range. The existence of crossover points seems to be a

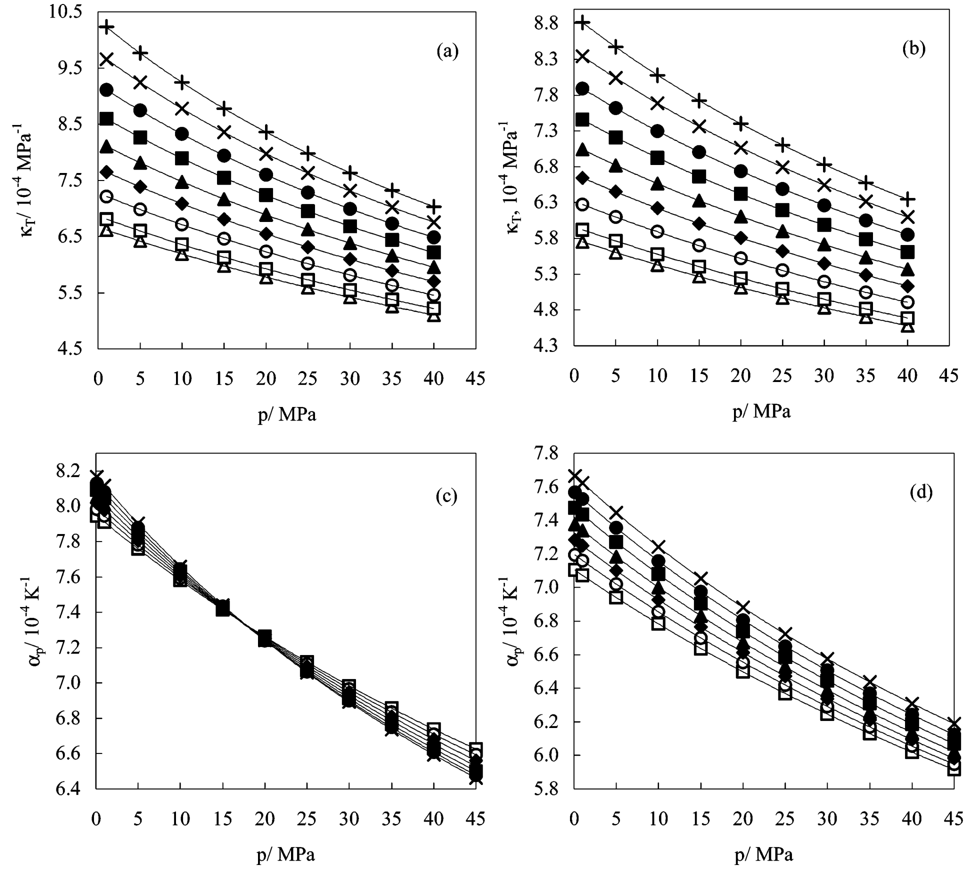

Figure 4. Isobaric thermal expansivities, α_p, and isothermal compressibilities, κ_T, for squalane (a, c) and PEB8 (b, d) vs the pressure and at different temperatures: △, 278.15 K; □, 283.15 K; ○, 293.15 K; ◆, 303.15 K; ▲, 313.15 K; ■, 323.15 K; ●, 333.15 K; ×, 343.15 K; +, 353.15 K.

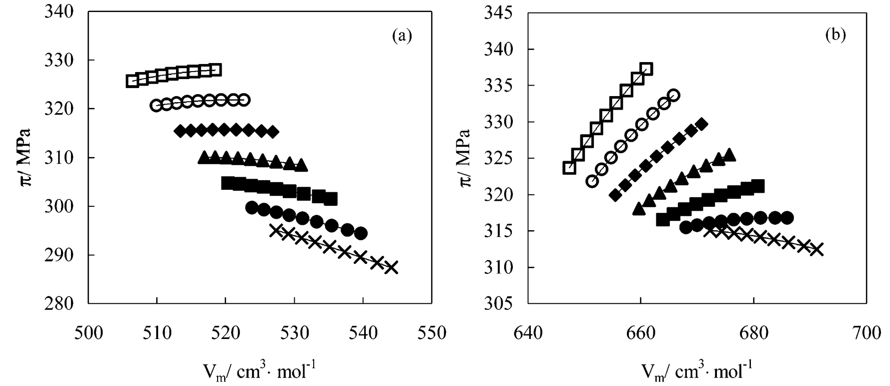

Figure 5. Internal pressure, π, against the molar volume for (a) squalane and (b) PEB8 at different temperatures: □, 283.15 K; ○, 293.15 K; ◆, 303.15 K; ▲, 313.15 K; ■, 323.15 K; ●, 333.15 K; ×, 343.15 K.

general property of the liquids.[36,37] The pressure at which α_p is independent of temperature (crossing point) is around 17 MPa for squalane. Randzio et al.,[36,38] who have also found this crossing point for hexane (65 MPa) and 1-hexanol (280 MPa), explain this behavior by assuming that a molecule in a dense liquid is confined by its closest neighbors and that the potential well in which the molecule oscillates changes shape with pressure. As a consequence of the intersection points, where $(\partial\alpha/\partial T)_p = 0$, the sign of the second derivative of the specific volume isobars will be different at low and at high pressures.[38] Furthermore, the crossing point is also related to the minimum of the isobaric heat capacity.[38]

Internal Pressure. Taking into account the expression $\pi = (\partial U/\partial V)_T = T(\partial p/\partial T)_V - p$, we obtained the internal pressure data, π, for squalane and PEB8 from eq 2, first by expressing p as a function of T and ρ and then by performing the analytical differentiation of this expression, obtaining

$$\left(\frac{\partial p}{\partial T}\right)_V = B'(T)\exp(f) - \frac{1}{\rho C}(B(T) + 0.1\ \text{MPa})\,\rho'(T, 0.1\ \text{MPa})\exp(f) - B'(T) \quad (7)$$

where $B'(T) = B_1 + 2B_2T$, $\rho'(T, 0.1\ \text{MPa}) = A_1 + 2A_2T$, and $f = [\rho(T, p) - \rho(T, 0.1\ \text{MPa}]/[C\rho(T, p)]$. The uncertainty of this property has been estimated to be ±3 MPa.

In Figure 5, the internal pressure of both compounds has been plotted against the molar volume. Contrary to the other studied derived properties, the internal pressure reaches higher values for PEB8 than for squalane. For squalane, from 313.15 to 343.15 K at constant temperature, this property diminishes with the molar volume (or increases with the pressure). Similar behavior has been found previously for several compounds such as monoethylene glycol alkyl ethers.[39] For PEB8, the trend in π with the molar volume is the opposite, thus a positive slope of the internal pressure with V_m is observed over all isotherms except at 343.15 K, for which the sign of the slope of the curve seemingly starts to change. Several compounds such as 2-butoxyethanol present this behavior.[40]

Conclusions

The densities of squalane and PEB8 in the temperature range from (283.15 K to 353.15) K and at pressures up to 45 MPa have been reported. The calibration procedure up to 45 MPa has been verified by comparing our density values of heptane with those previous reported by other authors finding good agreement (average absolute deviations of 0.02% and 0.05%). A correction factor on density due to the sample viscosity has been estimated. This factor ranges from 1×10^{-4} to 1×10^{-3} g·cm^{-3} for PEB8 and from 4×10^{-5} to 6×10^{-4} g·cm^{-3} for squalane**.** The pressure and temperature dependencies of squalane and PEB8 densities can be accurately represented by eq 2, which was then used to calculate isothermal compressibilities and isobaric thermal expansivities. These derived properties have also been estimated from other density correlations over isotherms (for κ_T) or isobars (for α_p), finding absolute deviations with the values estimated using eq 2 lower than $\pm 0.05 \times 10^{-4}$ MPa^{-1} and $\pm 0.03 \times 10^{-4}$ K^{-1} for squalane and $\pm 0.1 \times 10^{-4}$ MPa^{-1} and $\pm 0.12 \times 10^{-4}$ K^{-1} for PEB8. It has been observed that squalane is slightly more compressible and expansible than PEB8.

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