Temperature and Pressure Dependence of Branched Pentaerythritol Ester Density

Laura Fedele,* Sergio Marinetti, Francesco Pernechele, Sergio Bobbo, and Mauro Scattolini

National Research Council, Institute of Construction Technologies, Division of Padova, Corso Stati Uniti 4, 35127 Padova, Italy

Synthetic lubricants, which seem to be the most compatible oils with new refrigerants, are generally mixtures of pure components. At the moment, the literature reports only few works concerning experimental measurements and modeling of the volumetric properties for these fluids. The present study was conceived to measure the $p\rho T$ behavior in the liquid phase of three branched pentaerythritol tetraalkyl esters (PEBMs), i.e. 2-methylbutyric ester oil (PEBM5), 2-methylpentanoic ester oil (PEBM6), and 2-methylhexanoic ester oil (PEBM7). They are commonly used as precursors for the commercial polyol ester (POE) lubricants. The measurements were executed by means of a vibrating tube densimeter along four isotherms, for $T = (283$ to $343)$ K and $p = (0$ to $17)$ MPa. The validation of the experimental procedure was made by measuring the density of liquid decane along six isotherms, for $T = (283$ to $333)$ K and $p = (0$ to $35)$ MPa, and comparing the results with the literature. A dedicated equation of state, derived from the Tait equation, was used to correlate the experimental density data for PEBMs and for decane. A procedure to evaluate saturation density was also defined.

Introduction

The problem of the new refrigerant's compatibility with synthetic oils is becoming of particular concern, and stating the necessity to choose the most appropriate lubricants for each new refrigerant, the availability of models able to describe the thermodynamic behavior of lubricants and of refrigerant + lubricant mixtures is essential. Generally, the few available literature data on lubricants refer to commercial oils, whose composition is generally not known, making difficult the regression of proper thermodynamic models able to predict mixture properties.

On this basis, a research program on the thermodynamic behavior of various precursors of the commercial oils has been started in our laboratory.[1–6] In this paper, compressed liquid density measurements of three branched pentaerythritol esters, i.e., 2-methylbutyric ester oil (PEBM5), 2-methylpentanoic ester oil (PEBM6), and 2-methylhexanoic ester oil (PEBM7), along four isotherms between (283.15 and 343.15) K from atmospheric pressure to 17 MPa, are presented.

A modified Tait equation was used to represent data in the experimental temperature and pressure ranges.

The employed experimental apparatus and procedure were validated by measuring a well-known high-boiling fluid, decane ($C_{10}H_{22}$), along six isotherms and comparing the obtained values to those found in the literature, obtaining an absolute average deviation in terms of density of about 0.05 %.

Experimental Section

Materials. Three different pure branched pentaerythritol esters (PEBMs), i.e., 2-methylbutyric ester oil (PEBM5, CASRN 25811-38-5), 2-methylpentanoic ester oil (PEBM6, CASRN 25811-39-6), and 2-methylhexanoic ester oil (PEBM7), were used for the present measurements. The CASRN for PEBM7 was not found.

Table 1. Oils Used in the Measurements

chemical name	(acronym)	chemical formula	molar mass g·mol^{-1}
2-methylbutyric ester oil	(PEBM5)	$C_{25}H_{44}O_8$	472.620
2-methylpentanoic ester oil	(PEBM6)	$C_{29}H_{52}O_8$	528.727
2-methylhexanoic ester oil	(PEBM7)	$C_{33}H_{60}O_8$	584.835

Each oil was obtained by combining an alcohol (pentaerythritol) with four equal alkyl-branched chains, derived from carboxylic acids characterized by a different number of carbon atoms (from 4 carbons for 2-methylbutyric ester oil to 6 carbons for 2-methylhexanoic ester oil). Figure 1 shows the chemical structure of the branched pentaerythritol alkyl esters.

The three pure esters were synthesized by Chemipan (Poland) on a laboratory scale with a declared purity higher than 98 %.

Decane ($C_{10}H_{22}$, CASRN 124-18-5) was supplied by Aldrich with a declared purity >99 %.

To eliminate the noncondensable gases, each sample was put under a vacuum and then used with no further purification. Table 1 shows some characteristics of the oils considered in this work.

Experimental Apparatus and Procedure. The compressed liquid density measurements for the above cited oils were performed by means of an apparatus whose main component is a stainless steel vibrating tube densimeter (Anton Paar DMA 512). The used experimental procedure is analogous to that described in Fedele et al.[1] Here, only the main points are briefly summarized.

These measurements are based on the correlation existing between the oscillation period of the hollow resonating stainless steel tube and the density of the fluid contained. Pressure is measured by means of a piezo resistive pressure gauge (Druck DPI 145) with a scale up to 35 MPa, endowed with two pressure sensors measuring the differential pressure and the atmospheric one, giving the absolute pressure as the sum of these two. The estimated experimental pressure uncertainty is 20 kPa. The temperature of the vibrating tube is controlled with a stability of 0.003 K by a PID control system. Temperature measurements

---

* Corresponding author. Tel.: +39 049 8295831. Fax: +39 049 8295728. E-mail: laura.fedele@itc.cnr.it.

10.1021/je800110r CCC: $40.75

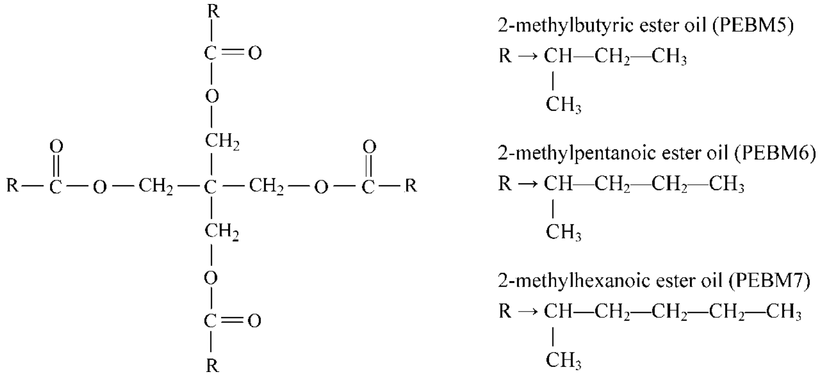

Figure 1. Chemical structure of the pentaerythritol tetraalkyl esters.

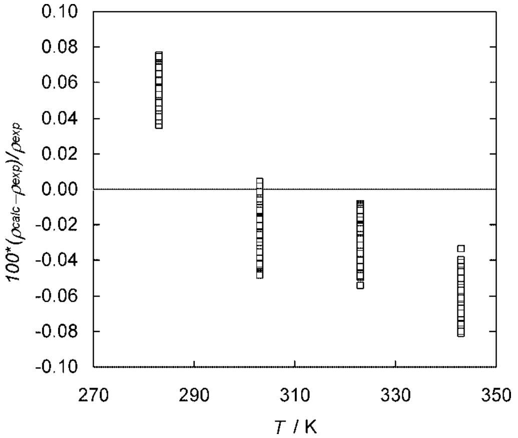

Figure 2. Deviations between the experimental and the calculated compressed liquid density data for PEBM5 from the modified Tait equation.[1]

are obtained by means of a Pt 100 Ω resistance thermometer, with an estimated uncertainty within 0.02 K.

After evacuating the measurement circuit, the oil is charged in the vibrating tube, while nitrogen is charged in the other part of the circuit. Then, oil and nitrogen are put in contact with the result that a meniscus is formed between the two fluids. Subsequently, the desired pressure of 17 MPa can be gradually reached pressurizing the nitrogen with a syringe pump (Isco Pump, model 260D) connected to the circuit. Even if no proper studies were made on solubility of nitrogen in oils, it is not a matter of concern considering that the meniscus is 0.9 m away from the vibrating tube and that nitrogen is an inert gas, with low diffusivity in oils. After stabilization of pressure and temperature, a controlled pressure bleeding of about (5 to 10) kPa·s^{-1} is performed expanding the volume inside the syringe pump and the values of vibrating tube period of oscillation continuously acquired. A dedicated software, developed in the LabView environment, allows the continuous acquisition and visualization of the main experimental parameters (period, temperature, and pressure) and the density calculation. The measurements of an isotherm take roughly 2 or 3 h, including time for the temperature change and stabilization. To change the oil, the cell must be open and clean. This operation takes at least 1 or 2 days.

Moreover, as a confirmation of the results, the experimental procedure was validated by measuring the compressed liquid density of a known fluid, such as decane.

Density Calibration. Accurate measurements require a proper calibration of the instrument, which consists of the determination of a correlation between the period of oscillation and the fluid density. For this purpose, it is necessary to measure the oscillation period of the U-tube under a vacuum and filled with a fluid of known density. Water was chosen as the calibrating fluid due to the high accuracy of the equation of state proposed by Wagner and Pruss.[7] Calibration is executed by measuring water density at the same experimental pressures and temperatures used, i.e., along four isotherms from (283.15 to 343.15) K up to 17 MPa. The correlations used for calibration are the same as those described in Fedele et al.[1]

Table 2. Selection of Experimental Compressed Liquid Density Values for PEBM5, PEBM6, and PEBM7 Evenly Sampled from all of the Data Sets

	T = 283.15 K		T = 303.15 K		T = 323.15 K		T = 343.15 K	
fluids	p / MPa	ρ / kg·m^{-3}	p / MPa	ρ / kg·m^{-3}	p / MPa	ρ / kg·m^{-3}	p / MPa	ρ / kg·m^{-3}
PEBM5	16.889	1033.6	16.878	1018.3	16.928	1003.5	16.820	988.7
	15.469	1032.6	15.466	1017.5	15.524	1002.6	15.413	987.6
	14.055	1031.9	14.055	1016.5	14.110	1001.6	14.008	986.6
	12.642	1031.1	12.652	1015.7	12.704	1000.7	12.592	985.5
	11.242	1030.1	11.248	1014.6	11.304	999.5	11.176	984.4
	9.838	1029.4	9.837	1013.8	9.903	998.6	9.771	983.4
	8.425	1028.5	8.432	1013.0	8.486	997.4	8.371	982.3
	7.011	1027.7	7.019	1011.8	7.073	996.7	6.958	981.1
	5.603	1026.7	5.610	1011.0	5.661	995.4	5.547	980.0
	4.186	1026.0	4.206	1010.0	4.261	994.5	4.137	978.9
	2.781	1025.1	2.797	1009.0	2.861	993.5	2.731	977.9
	0.101	1023.2	0.102	1007.3	0.102	991.2	0.102	975.6
PEBM6	16.552	1008.6	16.714	994.0	16.705	979.9	16.387	965.2
	15.140	1007.7	15.309	993.2	15.293	978.7	14.979	964.3
	13.737	1007.0	13.908	992.1	13.879	977.9	13.567	963.2
	12.334	1006.0	12.506	991.4	12.472	976.8	12.161	962.1
	10.930	1005.2	11.095	990.5	11.059	975.8	10.761	961.1
	9.520	1004.3	9.684	989.5	9.651	974.9	9.347	959.9
	8.118	1003.6	8.277	988.6	8.250	973.8	7.943	958.8
	6.715	1002.7	6.873	987.7	6.839	972.8	6.542	957.9
	5.309	1001.9	5.458	986.7	5.426	971.7	5.134	956.7
	3.897	1001.0	4.055	985.9	4.017	970.8	3.726	955.5
	2.484	1000.2	2.654	984.8	2.614	969.6	2.319	954.4
	0.103	998.6	0.103	983.2	0.105	967.7	0.498	952.9
PEBM7	16.675	993.9	16.451	979.6	16.630	965.7	16.689	951.7
	15.272	993.1	15.032	978.6	15.217	964.8	15.285	950.6
	13.860	992.3	13.620	977.8	13.810	963.7	13.881	949.7
	12.448	991.5	12.210	977.0	12.402	962.7	12.479	948.7
	11.034	990.9	10.795	976.0	10.991	961.8	11.059	947.4
	9.626	989.9	9.376	975.1	9.587	960.8	9.652	946.6
	8.218	989.1	7.962	974.2	8.171	959.8	8.249	945.6
	6.814	988.3	6.547	973.3	6.760	958.7	6.837	944.4
	5.412	987.5	5.139	972.4	5.352	957.8	5.425	943.4
	3.996	986.5	3.730	971.4	3.946	956.8	4.009	942.2
	2.579	985.7	2.328	970.5	2.534	955.8	2.608	941.2
	0.101	984.2	0.102	969.1	0.102	954.1	0.101	939.0

Only considering the uncertainty in pressure, temperature, and oscillation period measurements and in the calibration equation, the estimated compressed liquid density uncertainty is 0.5 kg·m^{-3}. In addition, as the present oils are quite viscous fluids, a correction should be done to the measured values of density, using the correction factor suggested by Anton Paar[8]

$$\frac{\rho_{\mathrm{exptl}}-\rho_{\mathrm{corr}}}{\rho_{\mathrm{exptl}}}=(-0.5+0.45\sqrt{\eta/\mathrm{mPa\cdot s}})\cdot 10^{-4} \qquad (1)$$

where ρ_{exptl} is the density value provided by the densimeter; ρ_{corr} is the corrected value including the viscosity effect; and η is the dynamic viscosity.

Unfortunately, viscosity data for the studied oils are not available in the literature, so this correction is not possible. Considering the already published viscosity data on other similar precursors of POE lubricants, i.e., pentaerythritol tetrapentanoate (PEC5) and pentaerythritol tetraheptanoate (PEC7),[9] this correction could range between (0.1 and 0.5) $\mathrm{kg\cdot m^{-3}}$, being higher at lower temperature and higher pressure. This systematic error should be added to the estimated compressed liquid density uncertainty, giving a total estimated uncertainty of 1 $\mathrm{kg\cdot m^{-3}}$.

Results and Discussion

Compressed Liquid Density. Experimental compressed liquid density data for the three PEBMs were measured along four isotherms in the temperature range from (283.15 to 343.15) K and pressure up to 17 MPa. A selection of the 14 675 measured data are summarized in Table 2. The complete data set is available on the web as Supporting Information.

To provide a valuable tool to calculate liquid density data for these PEBMs, the experimental values were regressed by means of a modified Tait equation. Indeed, for these oils, the literature lacks information about saturation molar volume V_{sat}, vapor pressure p_{sat}, and critical pressure and temperature, indicated as p_{c} and T_{c}, respectively. Then, it is not possible to employ the original Tait equation[10] at a given temperature in the form

$$V/\mathrm{m^3\cdot kmol^{-1}}=(V_{\mathrm{sat}}/\mathrm{m^3\cdot kmol^{-1}})\cdot\left(1-c\ln\frac{\beta+p/\mathrm{kPa}}{\beta+p_{\mathrm{sat}}/\mathrm{kPa}}\right) \qquad (2)$$

where V is the molar volume and p is the pressure.

Moreover, in eq 2, the parameter β is commonly expressed as

$$\beta=p_{\mathrm{c}}(-1+a(1-T_{\mathrm{r}})^{1/3}+b(1-T_{\mathrm{r}})^{2/3}+d(1-T_{\mathrm{r}})+e(1-T_{\mathrm{r}})^{4/3}) \qquad (3)$$

$$e=\exp(f+g\omega+h\omega^2) \qquad (4)$$

$$c=j+k\omega \qquad (5)$$

where $T_{\mathrm{r}}=T/T_{\mathrm{c}}$ is the reduced temperature and ω is the acentric factor.

First, the two-stage procedure proposed by Fedele et al.[1] was used to regress the experimental data. While, in the first stage, the residual errors of each isotherm data set were unbiased, the final errors exhibited a temperature-dependent bias, as shown in Figure 2. This problem was not encountered for PECs. Although a detailed analysis is beyond the scope of this paper, a possible explanation is the presence of multiple local minima in the first regression step that may provide different parameter sets fitting the data nearly equally well.

For this reason, the authors propose a single-stage regression based on a slightly modified Tait equation. All the isotherms of the same oil were regressed together, as a unique set. For the V_{sat} representation, a quadratic polynomial function of temperature was employed, a linear dependence not being satisfactory. Moreover, given the low saturation pressure of oils and the high values of β (always higher than 10^4), p_{sat} from 2 was neglected. Finally, to well describe β, the authors started from eq 3, finding that a quadratic dependence on $\sqrt[3]{(T/\mathrm{K})}$ was sufficient. On the basis of these hypotheses, eq 2 was modified as follows

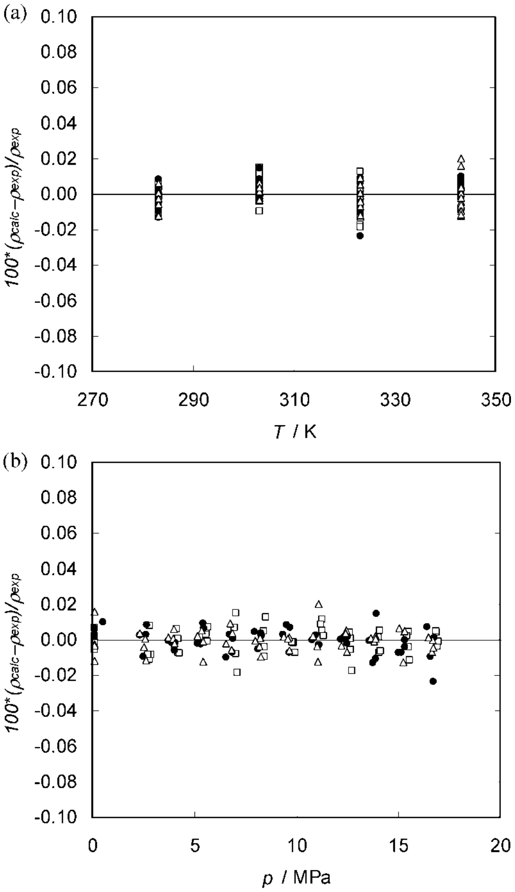

Figure 3. Deviations between the experimental selected and the calculated compressed liquid density data for the oils from eq 6 as a function of temperature (a) and pressure (b). □, PEBM5; ●, PEPM6; Δ, PEBM7.

$$V/\mathrm{m^3\cdot kmol^{-1}}=V_{\mathrm{sat}}\cdot\left(1-c\ln\frac{(\beta_2\cdot\sqrt[3]{(T/\mathrm{K})^2}+\beta_1\cdot\sqrt[3]{T/\mathrm{K}}+\beta_0)+p/\mathrm{kPa}}{(\beta_2\cdot\sqrt[3]{(T/\mathrm{K})^2}+\beta_1\cdot\sqrt[3]{T/\mathrm{K}}+\beta_0)}\right) \qquad (6)$$

where

$$V_{\mathrm{sat}}/\mathrm{m^3\cdot kmol^{-1}}=V_{\mathrm{sat2}}\cdot T^2+V_{\mathrm{sat1}}\cdot T+V_{\mathrm{sat0}} \qquad (7)$$

For each isotherm, density is represented by the equation

$$\rho=\frac{MM}{V} \qquad (8)$$

where $\rho/\mathrm{kg\cdot m^{-3}}$ is the density and $MM/\mathrm{g\cdot mol^{-1}}$ is the molar mass.

For each oil, all the density measurements were regressed by means of an overall least-squares fit, obtaining the seven coefficients V_{sat2}, V_{sat1}, V_{sat0}, β_2, β_1, β_0, and c. The β estimation in the form

$$\beta=(\beta_2\cdot\sqrt[3]{(T/\mathrm{K})^2}+\beta_1\cdot\sqrt[3]{T/\mathrm{K}}+\beta_0) \qquad (9)$$

was a weak point of the regression, being still dependent on the starting point value. For this reason, the first guess for β was calculated by means of 2, where p_{sat} was neglected, V_{sat} was approximated to the molar volume at the lower experimental pressure (generally, 1 bar), and c was fixed to 0.08 (the most

Table 3. Coefficients of Equations 6 and 7 and Deviation between the Experimental and the Calculated Data for PEBMs and Decane[a]

	2	1	0	AAD(|Δρ|) / kg·m^{-3}	AAD(|Δρ$_{perc}$|)	Max(|Δρ$_{perc}$|)
			PEBM5			
V_{sat}	$1.6227\cdot10^{-7}$	$2.7493\cdot10^{-4}$	$3.7103\cdot10^{-1}$	0.05	0.01	0.03
β	2.5906	$-2.2137\cdot10^{3}$	$5.4942\cdot10^{5}$			
c			$8.1609\cdot10^{-2}$			
			PEBM6			
V_{sat}	$2.4035\cdot10^{-7}$	$2.7671\cdot10^{-4}$	$4.3186\cdot10^{-1}$	0.05	0.01	0.03
β	2.2435	$-2.0215\cdot10^{3}$	$5.2295\cdot10^{5}$			
c			$8.2097\cdot10^{-2}$			
			PEBM7			
V_{sat}	$2.4618\cdot10^{-7}$	$3.2251\cdot10^{-4}$	$4.8318\cdot10^{-1}$	0.05	0.01	0.02
β	2.9679	$-2.4738\cdot10^{3}$	$5.9492\cdot10^{5}$			
c			$8.2827\cdot10^{-2}$			
			Decane			
V_{sat}	$2.8902\cdot10^{-7}$	$3.3331\cdot10^{-5}$	$1.6034\cdot10^{-1}$	0.05	0.01	0.05
β	1.0733	$-1.1744\cdot10^{3}$	$3.3142\cdot10^{5}$			
c			$8.6033\cdot10^{-2}$			

[a] N_p = number of points. $\mathrm{AAD}(|\Delta\rho|) = \sum_{i=1}^{N_p} |\rho_{calcd} - \rho_{exptl}| / N_p$ $\mathrm{AAD}(|\Delta\rho_{perc}|) = 100\cdot\sum_{i=1}^{N_p} |\rho_{calcd} - \rho_{exptl} / \rho_{exptl}| / N_p$ $\mathrm{Max}(|\Delta\rho_{perc}|) = \mathrm{Max}(100\cdot|\rho_{calcd} - \rho_{exptl} / \rho_{exptl}|)$.

common value for this kind of fluid). The initial estimate was taken as the average of all the calculated values from eq 2 at the different experimental pressures.

Table 3 reports all the regressed parameters of eq 6, and Figure 3 shows the deviations between selected experimental data and the equation. The absolute average deviation (AAD) between the calculated and the experimental data was about 0.01 %, with a maximum deviation around 0.03 %.

Furthermore, as a confirmation of this model, a different modified Tait equation was used to correlate the data, where β was expressed as a fourth-degree polynomial in $\sqrt[3]{(T/\mathrm{K})}$ to maintain its original form (eq 3). It was found that the results of this regression were similar to those found with eq 6. In conclusion, the employment of two additional parameters did not provide a significant improvement in the correlation, the absolute average deviation (AAD) always being 0.01 %.

Saturated Liquid Density Evaluation. Maintaining the physical meaning of the Tait equation, it is possible to estimate the saturated liquid density directly from eq 7. In Table 4 the calculated saturated liquid densities are shown.

Isothermal Compressibility and Isobaric Thermal Expansivity. Differentiating eq 6, and taking into account eqs 7, 8, and 9, it is possible to derive the isothermal compressibility and the isobaric thermal expansivity, according to their definitions, i.e., $\kappa_T = (1/\rho)(\partial\rho/\partial p)_T$ and $\alpha_p = -(1/\rho)(\partial\rho/\partial p)_p$.

Thus, these properties could be expressed as follows

$$\kappa(T,p) = \frac{c}{(\beta + p/\mathrm{kPa})\cdot\left(1 - c\ln\dfrac{\beta + p/\mathrm{kPa}}{\beta}\right)} \qquad (10)$$

$$\alpha(T,p) = \frac{1}{V_{sat}/\mathrm{kg\cdot kmol^{-1}}}\cdot\frac{\partial V_{sat}}{\partial T} + \frac{c\cdot p/\mathrm{kPa}}{(\beta^2 + \beta\cdot p/\mathrm{kPa})\cdot\left(1 - c\ln\dfrac{\beta + p/\mathrm{kPa}}{\beta}\right)}\cdot\frac{\partial\beta}{\partial T} \qquad (11)$$

where V_{sat}, β, and the relative derivative terms are calculated from eqs 8 and 9 using, as for c, the coefficients resulting from the regressions.

For each isotherm, five values of κ_T and α_p, respectively, were calculated for the three PEBMs at fixed pressure steps. The calculated data are presented in Table 5.

Table 4. Saturated Liquid Density Data for PEBM5, PEBM6, and PEBM7 Calculated through Equation 7

fluids	T/K	ρ_{sat}/kg·m^{-3}
PEBM5	283.15	1023.2
	303.15	1007.1
	323.15	991.2
	343.15	975.5
PEBM6	283.15	998.6
	303.15	983.1
	323.15	967.7
	343.15	952.5
PEBM7	283.15	984.2
	303.15	968.9
	323.15	953.9
	343.15	939.0

Validation of Density Measurements. Since $p\rho T$ data for these oils have not been reported in the literature to our knowledge, a direct validation of the results presented in this work is not possible. To overcome this problem, a series of compressed liquid density measurements were performed with the same experimental methodology for a fluid of known properties, and the data were regressed with the same applied model. Decane was chosen for its very low vapor pressure, comparable to that of oils. $p\rho T$ behavior of decane was investigated in the compressed liquid region along six isotherms between (283.15 and 333.15) K up to a pressure of 35 MPa. The correction due to viscosity to the measured density values is not necessary because, in the experimental temperature and pressure ranges, decane has a viscosity lower than 1.5 mPa·s, resulting in a negligible contribution to density through eq 1. 8773 points were measured, and the sets of experimental data are available on the web in the Supporting Information.

All the data were regressed by means of eq 6, and the parameters of the fitting equation are presented in Table 3. This equation represents the measured data well, the absolute average deviation (AAD) being 0.01 %.

A selection of the available literature compressed liquid density data[11–14] was compared with the regressed modified Tait equation, in the experimental temperature and pressure ranges. All the measured data are well represented by this equation, as indicated in Figure 4, the AAD for the data from Zúñiga-Moreno et al.[11] being 0.01 %, from Audonnet and Pádua[12] being 0.07 %, from Bessières at al.[13] being 0.08 %, and from Troncoso et al.[14] being 0.05 %.

Table 5. Calculated κ_T and α_p through Equations 10 and 11, Respectively, for PEBMs and Decane

	$T = 283.15$ K		$T = 303.15$ K		$T = 323.15$ K	
p MPa	$10^4\ \kappa_T$ MPa^{-1}	$10^4\ \alpha_p$ K^{-1}	$10^4\ \kappa_T$ MPa^{-1}	$10^4\ \alpha_p$ K^{-1}	$10^4\ \kappa_T$ MPa^{-1}	$10^4\ \alpha_p$ K^{-1}
			PEBM5			
17.0	5.60	7.40	6.19	7.37	6.80	7.37
15.0	5.67	7.45	6.27	7.44	6.90	7.43
10.0	5.85	7.61	6.50	7.60	7.18	7.60
5.0	6.05	7.77	6.74	7.77	7.48	7.77
0.1	6.26	7.94	7.00	7.95	7.80	7.96
			PEBM6			
17.0	5.63	7.25	6.23	7.25	6.87	7.27
15.0	5.70	7.30	6.32	7.32	6.98	7.33
10.0	5.88	7.46	6.54	7.48	7.26	7.51
5.0	6.08	7.62	6.79	7.66	7.56	7.70
0.1	6.29	7.79	7.05	7.85	7.89	7.90
			PEBM7			
17.0	5.60	7.20	6.22	7.21	6.85	7.24
15.0	5.67	7.26	6.30	7.27	6.95	7.31
10.0	5.85	7.42	6.53	7.44	7.23	7.47
5.0	6.05	7.59	6.77	7.62	7.53	7.66
0.1	6.25	7.77	7.03	7.81	7.85	7.85
			Decane			
34.0	7.45	8.52	8.23	8.61	9.11	8.61
30.0	7.68	8.67	8.52	8.78	9.47	8.80
20.0	8.35	9.10	9.34	9.27	10.49	9.36
10.0	9.15	9.60	10.35	9.85	11.77	10.05
0.1	10.12	10.20	11.61	10.58	13.43	10.93

Then, saturated liquid density data were calculated for decane both extrapolating each measured isotherm to the saturated pressure and derived through eq 7. For every temperature, ρ–p data were correlated by means of a fitting third-degree polynomial and then extrapolated to vapor pressures, calculated from the Refprop database.[15] In Table 6, all the calculated saturated liquid densities are shown. The two methods used to estimate the saturated liquid density for decane are substantially equivalent, since their maximum percentage deviation is −0.04 %.

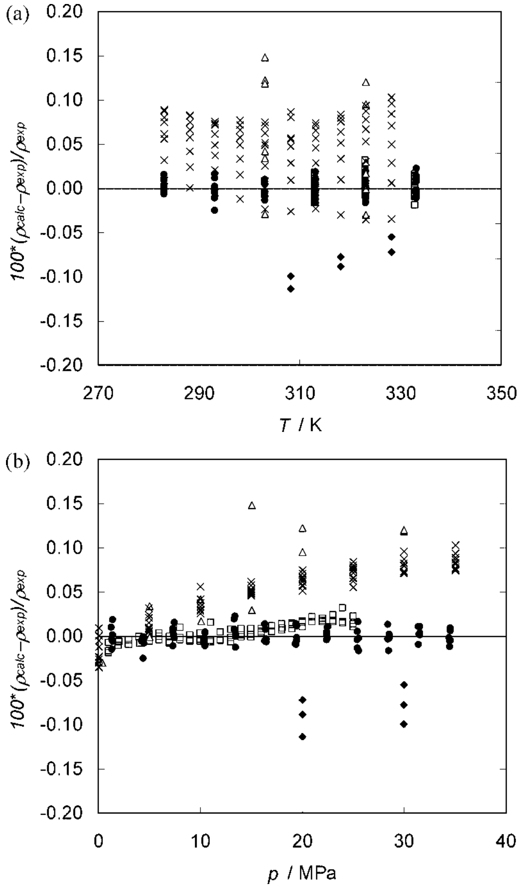

Figure 4. Deviations between the experimental and the calculated compressed liquid density data for decane from eq 6 as a function of temperature (a) and pressure (b). ●, present work; □, Zúñiga-Moreno et al.; Δ, Audennet et al.; ◆, Bessières et al.; ×, Troncoso et al.

Table 6. Comparison between the Two Methods Used for the Calculation of Saturated Liquid Density for Decane

	Refprop[15]	from eq 7	from extrapolation	
T/K	p_{sat}/MPa	ρ_{sat}/kg·m^{-3}	ρ_{sat}/kg·m^{-3}	$\Delta\rho_{perc}$
283.15	0.00006	737.4	737.3	−0.01
293.15	0.00013	729.8	729.6	−0.03
303.15	0.00026	722.2	721.9	−0.04
313.15	0.00049	714.5	714.6	0.01
323.15	0.00088	706.8	706.9	0.01
333.15	0.00152	699.1	699.2	0.02

$\Delta\rho_{perc} = 100 \cdot \rho_{ext} - \rho_{eq\ 7} / \rho_{eq\ 7}$.

Table 7. Saturated Liquid Density Data for Decane

T/K	from eq 7	Refprop[15]	$\Delta\rho_{perc}$	Cibulka et al.[16]	$\Delta\rho_{perc}$
283.15	737.4	738.1	0.10	737.5	0.01
293.15	729.8	730.3	0.06	730.0	0.02
303.15	722.2	722.6	0.05	722.4	0.03
313.15	714.5	714.8	0.04	714.8	0.04
323.15	706.8	707.0	0.02	707.2	0.05
333.15	699.1	699.2	0.02	699.5	0.06

$\Delta\rho_{perc} = 100 \cdot \rho_{lit.} - \rho_{eq\ 7} / \rho_{eq\ 7}$.

The data calculated through eq 7 were also compared with Refprop and literature data from Cibulka.[16] The resulting agreement is satisfactory, as shown in Table 7, confirming the reliability of eq 7, the AAD being 0.05 % and 0.04 % with data from Refprop and from Cibulka, respectively.

Moreover, as for PEBMs, for each isotherm, five values of κ_T and α_p, respectively, were calculated for decane at fixed pressure intervals and presented in Table 5. These calculated data were compared with those available in the literature,[14] as a confirmation of the results, giving a good agreement. The absolute average percentage deviations between the calculated and literature data are 1.5 % and 0.75 % for κ_T and α_p, respectively.

Conclusions

An experimental investigation of volumetric properties for three commercial POE oils precursors, PEBM5, PEBM6, and PEBM7, was performed by means of an apparatus based on a vibrating tube densimeter with a continuous data acquisition along four isotherms starting from an initial pressure of about 17 MPa. All the measured values were correlated using a dedicated equation derived from the generalized Tait equation, when the fluid vapor pressure is low, i.e., lower than atmospheric pressure. The same equation allowed the evaluation of the saturated liquid density. To validate all the employed experimental procedures, compressed liquid density data for a known fluid such as decane were measured, considering no data about the studied oils have been published in the literature to our knowledge. A good agreement with the literature data was achieved. Moreover, saturated liquid density data were calculated for decane, proving the reliability of eq 9 for the saturated density calculation.

Supporting Information Available:

All the experimental data. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Fedele, L.; Marinetti, S.; Bobbo, S.; Scattolini, M. *PρT* experimental measurements and data correlation of Pentaerythritol esters. *J. Chem. Eng. Data* **2007**, *52*, 108–115.

(2) Bobbo, S.; Scattolini, M.; Camporese, R.; Fedele, L.; Stryjek, R. Solubility of Carbon Dioxide in Pentaerythritol Esters Proc. ; *IIR International Conference - Thermophysical Properties and Transfer Processes of Refrigerants*, Vicenza, Italy, August 31−September 2, 2005.

(3) Bobbo, S.; Fedele, L.; Stryjek, R. Oil Structure Influence on the Solubility of Carbon Dioxide in POE Lubricants, *Proc. 11th International Refrigeration and Air Conditioning Conference at Purdue*, Purdue University, West Lafayette, IN (USA), July 17−20, 2006.

(4) Bobbo, S.; Scattolini, M.; Camporese, R.; Fedele, L.; Stryjek, R. Solubility of Carbon Dioxide in Some Commercial Poe Oils, *Proc 7th IIR Gustav Lorentzen Conference on Natural Working Fluids*, Trondheim, Norway, May 28−31, 2006.

(5) Bobbo, S.; Fedele, L.; Scattolini, M.; Camporese, R.; Stryjek, R. Solubility of carbon dioxide in 2-methylbutyric, 2-methylvaleric and 2-methylhexanoic ester oils. *Fluid Phase Equilib.* **2007**, *256*, 81–85.

(6) Bobbo, S.; Fedele, L.; Pernechele, F.; Stryjek, R. Correlation of solubility data of carbon dioxide in POE lubricants. *Proc. The 22nd IIR International Congress of Refrigeration - Refrigeration Creates the Future,* Beijing, China, August 21−26, 2007.

(7) Wagner, W.; Pruss, A. The IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use. *J. Phys. Chem. Ref. Data* **2002**, *31*, 387–535.

(8) Anton Paar GmbH, private communication.

(9) Pensado, A. S.; Comunãs, M. J. P.; Fernández, J. Relationship between Viscosity Coefficients and Volumetric Properties: Measurements and Modeling for Pentaerythritol Esters. *Ind. Eng. Chem. Res.* **2006**, *45*, 9171–9183.

(10) Thomson, G. H.; Brobst, K. R.; Hankinson, R. W. An Improved Correlation for Densities of Compressed Liquids and Liquid Mixtures. *AIChE J.* **1982**, *28*, 671–676.

(11) Zúñiga-Moreno, A.; Galicia-Luna, L. A.; Camacho-Camacho, L. E. Compressed Liquid Densities and Excess Volumes of CO_2 + Decane Mixtures from (313 to 363) K and Pressures up to 25 MPa. *J. Chem. Eng. Data* **2005**, *50*, 1030–1037.

(12) Audonnet, F.; Pádua, A. A. H. Viscosity and density of mixtures of methane and *n*-decane from 298 to 393 K and up to 75 MPa. *Fluid Phase Equilib.* **2004**, *216*, 235–244.

(13) Bessières, D.; Saint-Guirons, H.; Daridon, J.-L. Volumetric Behavior of Decane + Carbon Dioxide at High Pressures. Measurement and Calculation. *J. Chem. Eng. Data* **2001**, *46*, 1136–1139.

(14) Troncoso, J.; Bessières, D.; Cerdeiriña, C. A.; Carballo, E.; Romanì, L. *pρTx* Data for the Dimethyl Carbonate + Decane System. *J. Chem. Eng. Data* **2004**, *49*, 923–927.

(15) Lemmon, E. W.; Huber, M. L.; Mc Linden, M. O. *Reference Fluid Thermodynamic and Transport Properties (REFPROP), NIST Standard Reference Database 23, Version 8.0*; Physical and Chemical Properties Division, National Institute of Standards and Technology: Boulder, CO 80305, 2007.

(16) Cibulka, I. Saturated liquid densities of 1-alkanols from C_1 to C_{10} and *n*-alkanes from C_5 to C_{16}: a Critical Evaluation of Experimental Data. *Fluid Phase Equilib.* **1993**, *89*, 1–18.

Received for review February 13, 2008. Accepted May 29, 2008.

JE800110R