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Density Measurements under Pressure for Mixtures of Pentaerythritol Ester Lubricants. Analysis of a Density−Viscosity Relationship[†]

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Most of the industrial applications of ester-based synthetic lubricants are performed at medium and high pressures, but in the case of viscosity and density, the existing studies are carried out mainly at atmospheric pressure. Lubricants are normally composed by several compounds; hence, it is interesting to know how the pressure and the temperature affect the volumetric properties of mixed pentaerythritol esters (PE). In this work, the densities of two binary mixtures of pentaerythritol tetra(2-ethylhexanoate), PEB8, with pentaerythritol tetrapentanoate, PEC5, or with pentaerythritol tetraheptanoate, PEC7, and of one multicomponent mixture containing several pentaerythritol esters have been measured at temperatures from 278.15 K to 353.15 K and at pressures up to 45 MPa, using a vibrating tube densimeter. A correction factor, due to the viscosity of the sample, was applied to the density experimental values. The uncertainty in the measured densities is estimated to be 0.2 $\text{kg}\cdot\text{m}^{-3}$. The composition of each mixture was chosen so that its kinematic viscosity at 313.15 K and atmospheric pressure was around $34\cdot10^{-6}$ $\text{m}^2\cdot\text{s}^{-1}$ (ISO VG32). The experimental data have been used to study the behavior and the influence of temperature and pressure on the isothermal compressibility, the isobaric thermal expansion coefficient, and the internal pressure. In addition, according to Roland et al. [*J. Chem. Phys.* **2006**, *125*, 124508], for the three mixtures and four pure PEs, we have found that the viscosity is a unique function of TV^{γ}, where the exponent γ is related to the steepness of the intermolecular repulsive potential.

Introduction

Polyol ester based lubricants (POEs) are one of the most significant kinds of synthetic lubricants.[1,2] Depending on the types of multifunctional alcohol and monofunctional acid precursors, a wide variety of synthetic POEs can be obtained; this allows the industry to produce *designer* molecules.[3] Polyol esters have no β-hydrogens which makes them thermally and chemically stable.[1] The most commonly used polyol esters have as an alcohol precursor pentaerythritol and trimethylolpropane. Pentaerythritol esters (PEs) are the family of ester synthetic lubricants manufactured by reacting pentaerythritol with one or a mixture of monocarboxylic acids, which can have a different molecule size and branching. The ester group directly affects the physical properties of a lubricant by lowering the volatility and raising the flash point. Strong dipole moments that bind the molecules of the lubricant together are responsible for these effects.[4] The dipole moments also improve the oil lubricity by adhering strongly to the metal surface at the friction point. The presence of the ester group also affects other properties, such as the thermal stability, hydrolytic stability, solvency, lubricity, and biodegradability.[1,4]

On the other hand, in recent years, there is a new urgency for environmental responsibility. This development has led to an increased need for functional fluids that are both biodegradable and low in toxicity. Most of the PEs can be considered as environmentally acceptable base lubricants. Therefore, PEs are being used in many application areas as compressor oils, refrigeration lubricants, metalworking fluid, jet engine lubricants, high-temperature chain oils, hydraulic fluids, and automotive gear oils.[1]

Several investigations have shown how some properties of the PE lubricants such as viscosity, density, or pour point depend on the size and the branching of their molecules.[1,2,4−8] Nevertheless, the studies of physical properties, such as viscosity or density, were performed mainly at atmospheric pressure[5,6,8−11] when most of the PE uses are performed at medium and high pressures. Thus, for instance, the performance of machine elements such as gears and roller bearings depends on lubricants that routinely are subjected to pressure. The film thickness depends mainly on the pressure−viscosity coefficient but also on the density−pressure relationship.[12,13] In addition, it has been shown that different compressibility behavior can produce significantly different results in the hydrodynamic pressure range. The load carrying capacity of the lubricated contact is especially sensitive to the compressibility behavior of the lubricant. This indicates the need for employing realistic density−pressure relations. To produce better predictions of cavitation regions, fractional film content, and pressure, more physical variables that are condition-dependent such as viscosity and density might be needed.[14] Furthermore, in refrigeration systems using HFCs or CO_2, the actual behavior of the PE lubricants should be known under the conditions pertaining in the compressor, to improve its reliability and efficiency and to get better formulations of PE lubricants. In addition, densities at different pressures are also needed to obtain the pressure dependence of the experimental dynamic viscosity of the lubricants.

With the aim of expanding the literature data[5,6,8−11] at atmospheric pressures, in previous papers, different volumetric properties of pure pentaerythritol tetra(2-ethylhexanoate),

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PEB8,[15,16] pentaerythritol tetrapentanoate, PEC5,[17] pentaerythritol tetraheptanoate, PEC7,[18] and pentaerythritol tetranonanoate, PEC9,[18] in a broad range of temperatures and pressures (up to 45 MPa) have been reported, as well as the dynamic viscosities of the same pure PEs[19,20] over the temperature range of 303.15 K to 353.15 K and the pressure range of 0.1 MPa to 60 MPa. Very recently, Fedele et al.[21] have reported density values of PEC5, PEC7, pentaerythritol tetrabutanoate, pentaerythritol hexanoate, and pentaerythritol octanoate from 283 K to 343 K and at pressures up to 35 MPa.

Ester-based synthetic lubricants are normally composed by several compounds. Hence, it is interesting to know how the pressure and the temperature affect the thermophysical properties of mixed pentaerythritol esters. Thus, the main objective of this work is the study of the dependence of the volumetric properties on pressure and temperature in the three PE mixtures. Pentaerythritol esters studied in the present work are a multicomponent mixture of several PEs, PEC5−C9, with kinematic viscosity at 313.15 K and 0.1 MPa around $34 \cdot 10^{-6}$ $m^2 \cdot s^{-1}$ (ISO VG32) of unknown composition and two binary mixtures of a carboxylic acid ester (PEC5 or PEC7) with PEB8. The compositions of these two last binary mixtures are 0.6670 PEB8 + 0.3330 PEC7 and 0.6911 PEB8 + 0.3089 PEC5, with their kinematic viscosity being close to that of PEC5−C9 at the same reference conditions. Densities of PE mixtures were measured from 278.15 K to 353.15 K and at pressures up to 45 MPa.

Experimental Section

Materials. Pentaerythritol tetra(2-ethylhexanoate), PEB8, was supplied by Nikkol Chemicals (puriss 99 %). Pentaerythritol tetraheptanoate, PEC7, and pentaerythritol tetrapentanoate, PEC5, were previously synthesized[17,18] (> 95 %). The multicomponent mixture of several PEs, named here as PEC5−C9, with VG32 was provided by Croda, and it is a mixture, with unknown composition, of different pentaerythritol esters. The PEC5−C9 mixture is 99.9 % pure (ester) and contains < 0.1 % antioxidant (additive).

All the 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. Both binary mixtures were prepared by weight using a precision digital Sartorius 210-P balance with an accuracy of $5 \cdot 10^{-5}$ g. The estimated uncertainty in the mole fraction is lower than 10^{-4}.

Apparatus and Procedure. The volumetric properties under pressure of the three mixtures of PEs (PEB8 + PEC5, PEB8 + PEC7, and PEC5−C9) were investigated using a vibrating tube densimeter technique.[22] The density measurement is based on the dependence between the period of oscillation of a fixed U-tube and its mass. Since their first appearance as density meters, these mechanical oscillators have proven to be one of the most versatile and accurate instruments for relative measurements. Its main limitation relies on the fact that there has been no possibility so far to transform them to absolute instruments, due to the lack of a correct modeling of its working equation. Thus, to obtain the density, it is necessary to know two characteristic parameters. In this work, these parameters were determined through the measuring of the oscillation period of a reference fluid and of the evacuated tube over the whole experimental range, following the method developed by Lagourette et al.[23] A classical reference fluid is water, for which precise density data are available as a function of T and P.[24]

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 cellblock was measured with a calibrated (ITS-90) Anton Paar CKT100 platinum resistance thermometer with an uncertainty of ± 0.01 K. The pressure was measured with an HBM-PE300 differential pressure gauge. This manometer was calibrated with an uncertainty of ± 0.02 MPa. Both the complete experimental equipment and the experimental procedure have been previously described in detail.[22]

An important feature concerning mechanical oscillator densimeters is the effect of the sample viscosity on the density measurements (especially with viscosities higher than 15 mPa•s). The viscosity values of the three PE mixtures studied in the present work have been measured in our laboratory[25] over a wide range of pressures and temperatures with a commercial rolling ball viscometer (Ruska 1602-830). From these measurements, it can be concluded that the viscosity values for the three mixtures are higher than 15 mPa•s in a main part of the experimental range of the present work. Therefore, the effect of the sample viscosity must be considered and a correction factor for density measurements is needed.

Several researchers[26,27] obtained the relative density increase, named correction factor, $\Delta\rho$, due to the sample viscosity for vibrating tube densimeters, but only for equipment at atmospheric pressure. From their results, it is concluded that the correction factor depends not only on the sample viscosity but also on the specific design of the oscillator tube. In previous work[15−18,28,29] and in this paper, the correction factor due to the viscosity, $\Delta\rho$, for DMA 512 P (Hastelloy C-276) from an equation recently recommended by Anton Paar is applied.[18,30] The range of validity of this equation is for viscosities lower than 100 mPa•s.[30] For viscosities higher than 400 mPa•s, the relative correction factor, i.e., $\Delta\rho/\rho$, becomes constant, taking the value of $5 \cdot 10^{-4}$. Between 100 and 400 mPa•s, the correction factor follows an intermediate behavior.

For the PE mixtures, the correction factor, $\Delta\rho$, obtained using literature viscosity values,[25] ranges from $1 \cdot 10^{-4}$ to $5 \cdot 10^{-4}$ $g \cdot cm^{-3}$ in the present experimental PT conditions. The estimated density uncertainty taking into account the uncertainties of the temperature, the pressure, the period of oscillation measurements for water, vacuum, and the studied liquid (seven-digit frequency counter), and the water density accuracy is $1 \cdot 10^{-4}$ $g \cdot cm^{-3}$. The additional uncertainty that results from the density corrections because of the viscosity was estimated[30] to be $1 \cdot 10^{-4}$ $g \cdot cm^{-3}$. So, the overall uncertainty of the corrected density values for these compounds over the studied experimental range, using an only significant digit, is estimated to be $2 \cdot 10^{-4}$ $g \cdot cm^{-3}$.

Results and Discussion

Densities. The experimental corrected density data (297 points) of the three PE mixtures (PEB8 + PEC7, PEB8 + PEC5, and PEC5−C9) are presented in Table 1 along nine isotherms and along eleven isobars at pressures up to 45 MPa. The data obtained without viscosity correction are available in the Supporting Information. The corrected $P\rho T$ values were fitted with the following modified Tammann−Tait equation[31]

$$\rho(T,P) = \frac{\rho(T,P_{\mathrm{ref}}(T))}{1 - C \ln\left(\dfrac{B(T) + P}{B(T) + P_{\mathrm{ref}}(T)}\right)} \qquad (1)$$

Table 1. Corrected Experimental Densities, ρ/g·cm^{-3}, for PEB8 + PEC5, PEB8 + PEC7, and PEC5−C9 at Different Pressures and Temperatures

	T/K								
P/MPa	278.15	283.15	293.15	303.15	313.15	323.15	333.15	343.15	353.15
PEB8 + PEC5									
0.10	0.9861	0.9823	0.9749	0.9677	0.9603	0.9530	0.9458	0.9385	0.9313
1.00	0.9866	0.9829	0.9754	0.9683	0.9609	0.9536	0.9464	0.9392	0.9320
5.00	0.9888	0.9852	0.9779	0.9708	0.9637	0.9564	0.9494	0.9423	0.9353
10.00	0.9916	0.9881	0.9808	0.9739	0.9669	0.9598	0.9529	0.9460	0.9391
15.00	0.9943	0.9908	0.9837	0.9768	0.9700	0.9631	0.9563	0.9495	0.9428
20.00	0.9969	0.9935	0.9865	0.9797	0.9730	0.9662	0.9596	0.9529	0.9464
25.00	0.9995	0.9961	0.9892	0.9826	0.9759	0.9693	0.9628	0.9563	0.9498
30.00	1.0019	0.9986	0.9918	0.9853	0.9787	0.9723	0.9658	0.9595	0.9531
35.00	1.0044	1.0011	0.9944	0.9879	0.9815	0.9751	0.9688	0.9625	0.9563
40.00	1.0067	1.0035	0.9969	0.9905	0.9842	0.9779	0.9717	0.9655	0.9594
45.00	1.0091	1.0058	0.9994	0.9931	0.9868	0.9806	0.9745	0.9684	0.9624
PEB8 + PEC7									
0.10	0.9777	0.9740	0.9668	0.9596	0.9524	0.9451	0.9380	0.9307	0.9237
1.00	0.9782	0.9745	0.9673	0.9602	0.9530	0.9457	0.9386	0.9314	0.9244
5.00	0.9805	0.9768	0.9697	0.9627	0.9557	0.9485	0.9416	0.9344	0.9276
10.00	0.9832	0.9797	0.9726	0.9658	0.9588	0.9518	0.9451	0.9381	0.9314
15.00	0.9859	0.9824	0.9755	0.9687	0.9619	0.9551	0.9484	0.9416	0.9350
20.00	0.9885	0.9851	0.9782	0.9716	0.9649	0.9582	0.9517	0.9450	0.9386
25.00	0.9910	0.9876	0.9809	0.9744	0.9678	0.9612	0.9548	0.9483	0.9419
30.00	0.9934	0.9901	0.9835	0.9771	0.9706	0.9641	0.9578	0.9514	0.9452
35.00	0.9958	0.9926	0.9861	0.9797	0.9733	0.9670	0.9608	0.9545	0.9484
40.00	0.9982	0.9950	0.9886	0.9823	0.9760	0.9697	0.9636	0.9575	0.9515
45.00	1.0005	0.9973	0.9910	0.9848	0.9786	0.9724	0.9664	0.9603	0.9544
PEC5−C9									
0.10	0.9889	0.9850	0.9774	0.9700	0.9625	0.9550	0.9477	0.9402	0.9329
1.00	0.9894	0.9856	0.9780	0.9706	0.9632	0.9557	0.9484	0.9410	0.9336
5.00	0.9917	0.9879	0.9804	0.9732	0.9659	0.9584	0.9513	0.9441	0.9369
10.00	0.9946	0.9909	0.9834	0.9763	0.9691	0.9618	0.9549	0.9478	0.9408
15.00	0.9973	0.9937	0.9864	0.9793	0.9723	0.9652	0.9584	0.9514	0.9445
20.00	1.0000	0.9964	0.9892	0.9822	0.9753	0.9683	0.9617	0.9549	0.9481
25.00	1.0025	0.9990	0.9919	0.9851	0.9783	0.9714	0.9649	0.9582	0.9516
30.00	1.0050	1.0016	0.9946	0.9878	0.9811	0.9744	0.9679	0.9614	0.9549
35.00	1.0075	1.0041	0.9972	0.9905	0.9839	0.9772	0.9709	0.9645	0.9581
40.00	1.0099	1.0065	0.9997	0.9931	0.9866	0.9800	0.9738	0.9675	0.9612
45.00	1.0122	1.0089	1.0022	0.9957	0.9892	0.9828	0.9767	0.9705	0.9642

where $\rho\ (T,P_{\text{ref}}(T))$ is the temperature dependence of the density of the fluid at the reference pressure and $P_{\text{ref}}(T) = 0.1$ MPa. Polynomial functions of temperature were used for $\rho\ (T, P_{\text{ref}}(T))$ and $B(T)$

$$\rho(T, 0.1\ \text{MPa}) = \sum_{i=0}^{m} A_i T^i \qquad (2)$$

$$B(T) = \sum_{j=0}^{n} B_j T^j \qquad (3)$$

The A_i values for the three fluids were determined smoothing eq 2 to the experimental densities at atmospheric pressure. The values of B_j and C have been determined by fitting eq 1 to all the experimental data at different pressures than the atmospheric one. The three sets of the fitting coefficient (A_i, B_j, C) values and the standard deviations (σ and σ^*) are listed in Table 2. The number of parameters A_i and B_j has been determined using an F-test.

Table 2. A_i, B_j, and C Coefficients and Standard Deviations, σ and σ^*, for Equations 1−3

	PEB8 + PEC5	PEB8 + PEC7	PEC5−C9
A_0/g·cm^{-3}	1.20091	1.17826	1.21361
$-10^3 A_1$/g·cm^{-3}·K^{-1}	0.80562	0.72128	0.85732
$10^6 A_2$/g·cm^{-3}·K^{-2}	0.11915	−	0.17689
$10^5\sigma$/g·cm^{-3}	5	8	7
B_0/MPa	452.4343	397. 2636	401.8332
$-B_1$/MPa·K^{-1}	1.5393	1.1965	1.2668
$10^3 B_2$/MPa·K^{-2}	1.454	0.925	1.074
C	0.080265	0.080066	0.079311
$10^5\sigma^*$/g·cm^{-3}	4	4	6

The experimental corrected densities for the PEB8 + PEC5, PEB8 + PEC7, and PEC5−C9 mixtures are plotted in Figure 1a against pressure together with the corresponding Tammann−Tait correlations. In this figure, it can be seen how, as usual, ρ increases when the temperature decreases or the pressure increases. In Figure 1b, the trend of densities of the three mixtures and pure PEs at 303.15 K against pressure can be observed. Pure[15−18] and mixed PEs present under the same PT conditions the following trend for density values: PEC5 > PEC7 > PEC5−C9 > PEB8 + PEC5 > PEB8 + PEC7 > PEB8 > PEC9; i.e., the densities of the three mixtures exhibit intermediate values between PEC7 and PEB8.

Derived Properties. From the $P\rho T$ relations (eqs 1−3), it is possible to evaluate the effect of both temperature and pressure on different thermophysical properties as isothermal compressibilities, κ_T, or isobaric thermal expansivities, α_p. These properties can be calculated from eq 1 and their definitions, $\kappa_T = -(1/V_m)(\partial V_m/\partial P)_T = (1/\rho)(\partial\rho/\partial P)_T$ and $\alpha_P = (1/V_m)(\partial V_m/\partial T)_P = -(1/\rho)(\partial\rho/\partial T)_P$. The uncertainties κ_T and α_P were estimated to be 1 % and 4 %, respectively, over the entire pressure and temperature ranges.[15]

In general, the values of the isothermal compressibility for the three PE mixtures are very similar (Table 3). κ_T presents relatively small values compared with other organic compounds.[32−36] The isothermal compressibility diminishes with the pressure along isotherms and increases with the temperature at constant pressure for the PE mixtures and for the pure PEs, as

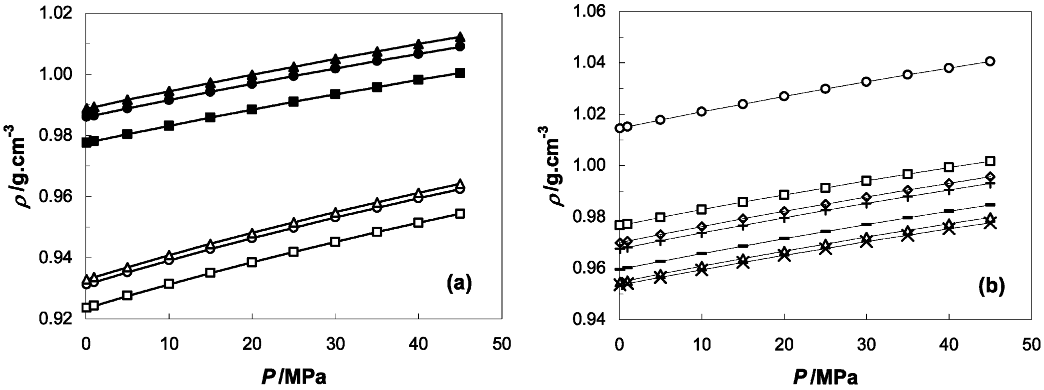

Figure 1. Experimental densities, ρ, vs pressure of (a) ●, ○, PEB8 + PEC5; ■, □, PEB8 + PEC7; and ▲, △, PEC5−C9, at 278.15 K (filled symbols) and 353.15 K (unfilled symbols). —, Tammanan−Tait correlations. Experimental densities, ρ, vs pressure of (b) ○, PEC5;[17] □, PEC7;[18] ◇, PEC5−C9; ×, PEC9;[18] +, PEB8 + PEC5; −, PEB8 + PEC7; △, PEB8,[15,16] at 303.15 K. —, polynomial fitting for guided-eye.

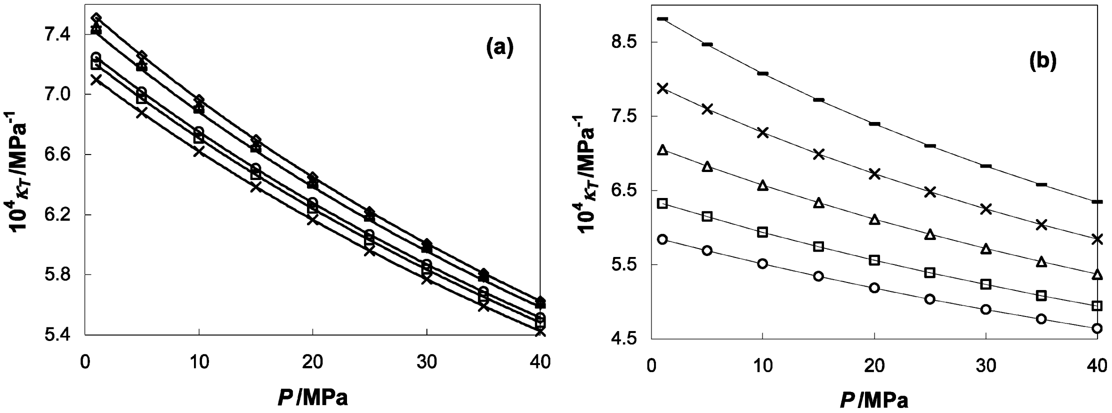

Figure 2. Isothermal compressibility, κ_T, of (a) ○, PEC5;[17] □, PEC7;[18] ◇, PEC5−C9; ×, PEC9;[18] +, PEB8 + PEC5; −, PEB8 + PEC7; and △, PEB8[15,16] vs pressure at 323.15 K and of (b) PEB8 + PEC5 at ○, 278.15 K; □, 293.15 K; △, 313.15 K; ×, 333.15 K; and −, 353.15 K vs pressure. —, polynomial fitting for guided-eye.

Table 3. Isobaric Thermal Expansivity, α_P, and Isothermal Compressibility, κ_T, at Several Temperatures, T, and Pressures, P, for PEB8 + PEC5, PEB8 + PEC7, and PEC5−C9

	$10^4\alpha_P$/K^{-1}			$10^4\kappa_T$/MPa^{-1}		
P/MPa	T = 283.15 K	T = 313.15 K	T = 343.15 K	T = 283.15 K	T = 313.15 K	T = 343.15 K
			PEB8 + PEC5			
0.10	7.51	7.61	7.71			
1.00	7.49	7.58	7.67	5.98	7.04	8.32
10.00	7.21	7.25	7.28	5.64	6.57	7.67
20.00	6.95	6.94	6.92	5.30	6.11	7.06
30.00	6.71	6.66	6.61	5.00	5.72	6.54
40.00	6.50	6.42	6.34	4.73	5.38	6.09
			PEB8 + PEC7			
0.10	7.41	7.57	7.75			
1.00	7.38	7.54	7.71	6.00	7.01	8.30
10.00	7.12	7.22	7.30	5.65	6.54	7.65
20.00	6.87	6.91	6.93	5.31	6.09	7.04
30.00	6.65	6.65	6.60	5.01	5.70	6.52
40.00	6.45	6.41	6.32	4.74	5.35	6.08
			PEC5−C9			
0.10	7.69	7.76	7.83			
1.00	7.66	7.72	7.78	6.09	7.12	8.39
10.00	7.40	7.40	7.40	5.73	6.63	7.71
20.00	7.14	7.10	7.03	5.37	6.16	7.09
30.00	6.92	6.83	6.72	5.06	5.75	6.56
40.00	6.71	6.60	6.45	4.79	5.40	6.11

can be seen in Figure 2. When increasing the temperature, the cohesion forces of molecules diminish because the increase of temperature favors the randomness of the distribution of molecules and increases the intermolecular distance and the free volume, which favors the compression of the liquid. Increasing pressure provokes the opposite effects, hence the liquid becomes less compressible. Nevertheless, it should be taken into account that pressure and temperature affect both contributions to the compressibility, $\kappa_T = -(1/V_m)(\partial V_m/\partial P)_T$. For each PE and for the PE mixtures, their κ_T behavior shows that the decrease of $[-(\partial V_m/\partial P)_T]$ with an increase in pressure (or a decrease in temperature) is enough to counteract the increase in V_m^{-1}.

Taking into account our previous studies on pure pentaerythritol esters,[15−18] the following trend is found for κ_T, over most

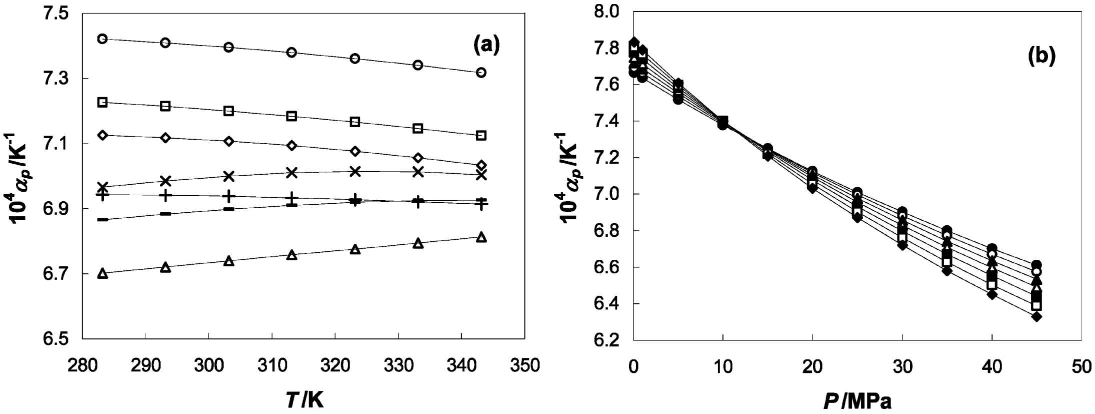

Figure 3. Thermal expansion coefficients, α_P, of (a) ○, PEC5;[17] □, PEC7;[18] ◇, PEC5−C9; ×, PEC9;[18] +, PEB8 + PEC5; −, PEB8 + PEC7; and △, PEB8[15,16] vs temperature at 20 MPa and of (b) PEC5−C9 vs temperature at: ●, 283.15 K; ○, 293.15 K; ▲, 303.15 K; △, 313.15 K; ■, 323.15 K; □, 333.15 K; ◆, 343.15 K. −, polynomial fitting for guided-eye.

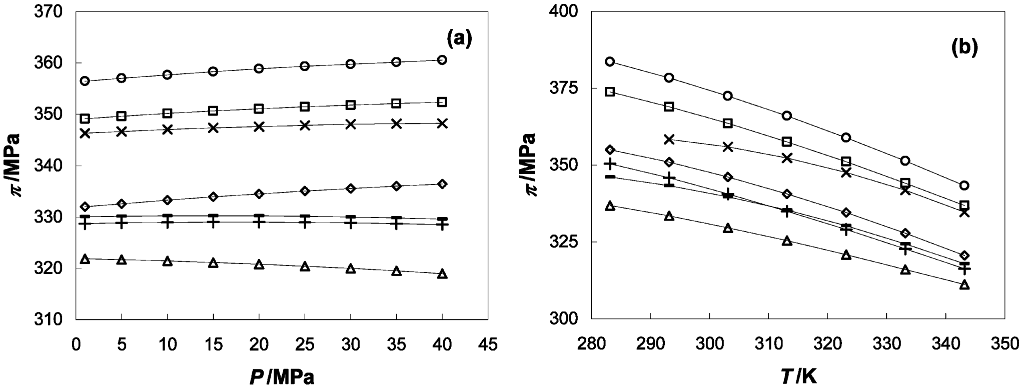

Figure 4. Internal pressure, π, (a) vs pressure at 323.15 K and (b) vs temperature at 20 MPa of ○, PEC5;[17] □, PEC7;[18] ◇, PEC5−C9; ×, PEC9;[18] +, PEB8 + PEC5; −, PEB8 + PEC7; and △, PEB8.[15,16]

of the *PT* conditions: PEC5−C9 > PEB8 > PEB8 + PEC5 > PEB8 + PEC7 > PEC5 > PEC7 > PEC9 (see Figure 2a). Then, PEC5−C9 is the more compressible fluid. For the binary mixtures PEB8 + PEC5 and PEB8 + PEC7, the κ_T values lie between those of the corresponding pure components. At the lower temperatures, mixtures containing PEB8 present very close values to those of PEB8, with the differences being of the same order as the uncertainty. In previous papers,[17,18] we have analyzed the effects of the length and the degree of branching of the acid chains of the PE molecules on the compressibility. In this sense, we must point out that the results obtained here are in agreement with those found previously.[17,18] Thus, the PEs with branching acid chains present higher compressibility values.

With respect to the isobaric thermal expansivity, its values for the three PE mixtures are quite similar and relatively small (see Table 3) in comparison with other organic compounds.[32−36] Taking into account our previous studies on pure pentaerythritol esters,[15−18] this property presents the following sequence: PEC5 > PEC7 > PEC5−C9 > PEC9 > PEB8 + PEC5 > PEB8 + PEC7 > PEB8 (Figure 3a). Hence, PEs with linear acid chains are more expandable than those with branching chains. For the binary mixtures PEB8 + PEC5 and PEB8 + PEC7, the α_P values are between those of the corresponding pure components. The multicomponent mixture PEC5−C9 is slightly more expandable and more compressible than the binary mixtures. For example, in Figure 3b the isobaric thermal expansivities for the multicomponent mixture PEC5−C9 are plotted against pressure at different temperatures. For the three PE mixtures, α_p decreases with increasing pressure. This is due to the observation that the capacity of a liquid to expand diminishes when the pressure increases, due to the diminution of free intermolecular space. For these mixtures, the decrease of $[(\partial V_m/\partial T)_P]$ with increasing pressure is large enough to counteract the increase of V_m^{-1}. On the other hand, as can also be seen in Figure 3b, the α_P isotherms have an intersection point inside the studied pressure range. The pressure at which α_P is independent of temperature (crossing point) is around 12 MPa for the PEC5−C9 mixture. This crossing point is also present in the case of the mixture PEB8 + PEC5 (around 17 MPa) and for PEB8+PEC7 (close to 25 MPa).

On the other hand, as we have previously[17,18] found, it is interesting to note that the branching of the chains affects the isothermal compressibility and the thermal expansion coefficient differently. Thus, the isothermal compressibility values of linear pentaerythritol esters are lower than those of PEs with branching chains,[15−18] contrary to the trend for α_P values. This is due to the fact that $[-(\partial V_m/\partial P)_T]$ values for PEB8 are quite larger than the expected values for its isomer with linear chains PEC8, whereas the opposite occurs for $(\partial V_m/\partial T)_P$.[17]

From the $P\rho T$ relations, we have estimated another property, the internal pressure, $\pi = (\partial U/\partial V)_T = T(\alpha_P/\kappa_T) - P$, which provides essential information on the intensity of intermolecular interactions. The uncertainty of this property has been estimated to be ± 3 MPa.[15] In Figure 4, the behavior of the internal pressure of the analyzed mixtures and the pure PEs[15−18] is shown. The trend found for π is PEC5 > PEC7 > PEC9 > PEC5−C9 > PEB8 + PEC7 > PEB8 + PEC5 > PEB8, except for temperatures lower or equal to 303.15 K, for which the internal pressure of the mixture PEB8 + PEC5 is higher than that of the mixture PEB8 + PEC7 (Figure 4b). This fact clearly indicates that the stronger molecular interactions are presented

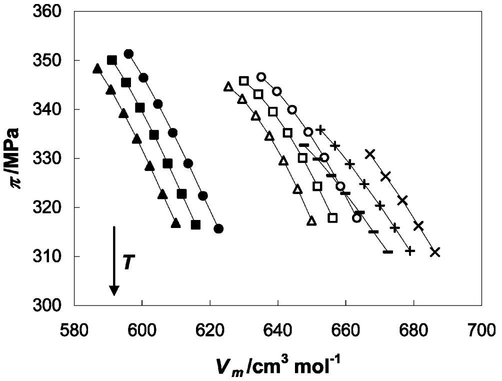

Figure 5. Internal pressure, π, vs molar volume, V_m, of PEB8 + PEC5 (●, 10 MPa; ■, 25 MPa; ▲, 40 MPa), PEB8 + PEC7 (○, 10 MPa; □, 25 MPa; △, 40 MPa), and PEB8[15,16] (×, 10 MPa; +, 25 MPa; −, 40 MPa), at temperatures from 283.15 K to 343.15 K at 10 K intervals.

in PEC5, as we pointed out before,[17] and the lower ones are presented in PEB8, as a result of the branching of the chains. For the binary mixtures PEB8 + PEC5 and PEB8 + PEC7, the π values are between those of the corresponding pure components.

For the three mixtures and the pure PEs, π decreases when temperature rises along isobars; i.e., $(\partial\pi/\partial T)_P < 0$, as can be seen in Figures 4b and 5. The behavior of internal pressure with temperature for several compounds has been studied by Kartsev et al.[37] These authors indicate that the derivative $(\partial\pi/\partial T)_P$ is related to the structural organization of fluids. Thus, according to the sign of the slope of the $\pi(T)$ curve, liquids can be classified in two structural groups: those fluids being $(\partial\pi/\partial T)_P < 0$, namely, non or weakly associated fluids, and those being $(\partial\pi/\partial T)_P > 0$, namely, the associated fluids, which have molecules linked by hydrogen bonds. For the last group, the greater the degree and the stability of the association, the larger the slope. Accordingly, in pure PEs and their mixtures, there are strong dipole−dipole interactions but not hydrogen bonds, and the values of $(\partial\pi/\partial T)_P$ are negative.

In previous work,[22,38] we have analyzed the behavior of internal pressure with molar volume. In these studies, as usual, the total intermolecular energy was considered as the sum of two separate contributions, such as the Mie potential.[34,39] If the internal potential energy is plotted against the molar volume for a Mie potential, a curve with a minimum and an inflection point is obtained.[38] For the smaller molar volumes, the slope of the curve $U(V_m)$ is negative, i.e., $\pi < 0$. For the molar volumes between those of the minimum and of the inflection point, the $U(V_m)$ is concave upward, the slope being positive. Thus, π is positive and increases with the molar volume. Finally, for volumes bigger than that of the inflection point, the $U(V_m)$ curve is concave downward; that is, π is positive, but it decreases when V_m increases. In Figure 5, we can observe the behavior of the $\pi(V_m)$ curves for the two binary PE mixtures together with that of PEB8. As can be observed, for the lower temperatures, at isothermal conditions, π rises with the molar volume, indicating that the molar volume is lower than that of the inflection point. For the higher temperatures, π remains almost constant, demonstrating that at these conditions the molar volume is close to that of the inflection point. Accordingly for PEB8[18,19] and the two binary mixtures, the trend of π with pressure along isotherms is slightly different at lower and higher temperatures. Nevertheless, for PEC5−C9, internal pressure values increase when pressure rises along all the isotherms.

Roland et al. Relation. Recently, Roland et al.[40] have shown the superposition of relaxation times, τ, for various glass-forming liquids and polymers when expressed as a function of TV^{γ}; that is, τ is a unique function of TV^{γ}

$$\tau(T,V) = f(TV^{\gamma}) \tag{4}$$

where the exponent γ is a material constant and V is the specific volume. In a very recent article, Roland et al.[41] extend this thermodynamic scaling of the relaxation times to the viscosity, η. That is, for a compound, η is only a functional of TV^{γ}

$$\eta(T,V) = \eta(T,p) = f(TV^{\gamma}) \tag{5}$$

The utility of the scaling is not only to interpolate and extrapolate experimental data but also to know the value of the exponent γ for a given liquid. According to Roland et al.,[40,41] this parameter reflects the magnitude of the intermolecular forces and the harmonic intramolecular bond stretching potential. In addition, the exponent γ links the thermodynamic and the transport behavior. Thus, Roland et al.[41] have verified eq 5 for several liquids. They have found decreasing γ values in going from van der Waals fluids ($\gamma = 8$ for octane) to ionic liquids ($\gamma = 2.25$ for 1-methyl-3-octylimidazolium tetrafluroborate), although for some strongly H-bonded materials, such as water, they have observed that the superpositioning fails.[41]

Thus, we have determined the exponent γ (eq 5) for pure PEs (PEC5, PEC7, PEC9, and PEB8) and the three mixtures presented in this work. For the pure PEs, densities and viscosities have been taken from our previous articles,[15−20] as well as the viscosities[25] for the three mixtures. We have limited the analysis

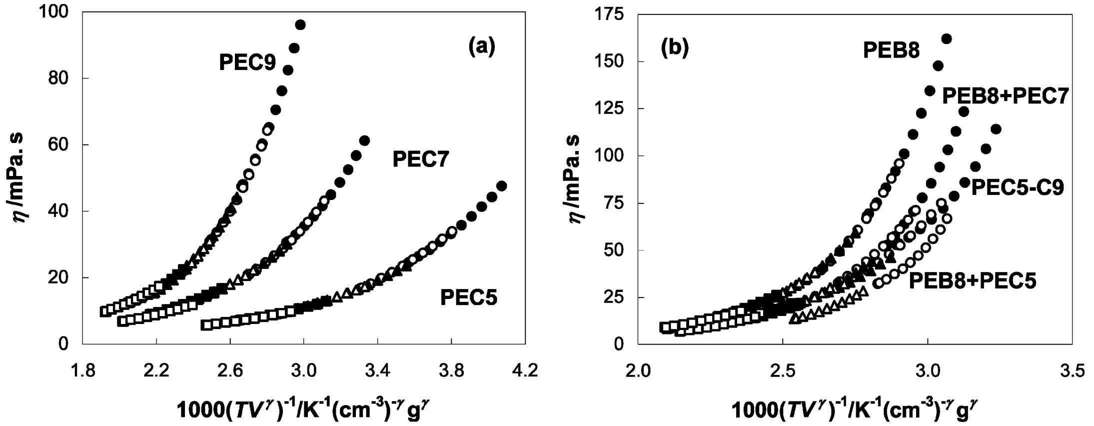

Figure 6. Superpositioned viscosities of (a) PEC5 ($\gamma = 5.3$), PEC7 ($\gamma = 5.4$), and PEC9 ($\gamma = 4.5$) and of (b) PEB8 ($\gamma = 3.6$), PEB8 + PEC5 ($\gamma = 3.0$), PEB8 + PEC7 ($\gamma = 3.5$), and PEC5−C9 ($\gamma = 4.3$). Symbols represent the different isotherms: ●, 303.15 K; ○, 313.15 K; ▲, 323.15 K; △, 333.15 K; ■, 343.15 K; □, 353.15 K. The pressure ranges from ambient to 45 MPa.

to the overlapping pressure and temperature ranges of both density and viscosity measurements.

For each PE, the viscosity data collapse onto a single master curve when plotted as a function of $(TV^{\gamma})^{-1}$ (Figure 6), for a given γ value. To obtain more precisely γ, we tried values stepped 0.1 and fitted different functionalities to the experimental data. The best regression coefficients were obtained using polynomial functions and with the γ value data detailed in the caption of Figure 6. The trend found for the scaling exponent γ is PEC7 > PEC5 > PEC9 > PEC5−C9 > PEB8 > PEB8 + PEC7 > PEB8 + PEC5; i.e., the highest value of γ (5.4) corresponds to PEC7, and the lowest one corresponds to the PEB8 + PEC5 mixture (3.0). These exponents are lower than the values for the van der Waals liquids[41] with low molecular weight, in agreement with the fact that these PEs are polar-branched and highly compact rigid molecules, and higher than those of hydrogen-bonded liquids. These values compare well with those found for Roland et al.[41] for another ester lubricant, dibutylphthalate ($\gamma = 3.2$), and for squalane ($\gamma = 4.2$).

It is interesting to note, as for the three pure PEs with linear acid chains, the sequence of γ is the inverse to that of the glass-transition temperatures, T_g, found by Shobha and Kishore.[6] At the glass-transition temperature, the molecular rotation is restricted, and below this temperature, the molecules cannot rotate and translate. Shobha and Kishore[6] have analyzed the dependence of T_g on molecular weight (M_W) in several esters, observing that for the pentaerythritol tetraalkyl esters T_g decreases with molecular weight until $M_W \approx 600$ g·mol^{-1} and increases sharply thereafter. Thus, the T_g trend is the following: PEC7 (584 g·mol^{-1}) < PEC5 (472 g·mol^{-1}) < PEC9 (696 g·mol^{-1}). The dependence of T_g on molecular weight was explained by these authors as being from the segmental motion.[6] Thus, as the molecular weight increases beyond 600 g·mol^{-1}, the flexibility of the chain will not be favored in branched compounds due to excessive branching that restricts the segmental motion, and hence T_g increases gradually as the molecular weight increases. Accordingly, Roland et al. have pointed out that, in the same manner that a flexible chain structure affects the glass-transition temperature, it could also affect the dependence of η on V (i.e., the γ values), although in general it is not possible to make a direct connection between chemical structure and γ.[41] In this sense, it should be indicated that the constancy of the product $T_g V_g^{\gamma}$ has conducted to eqs 4 and 5. We have also determined these exponents considering only the density and viscosity data at 0.1 MPa, obtaining practically the same γ values. So, as Roland et al. have pointed out,[40] their scaling relation can be used to determine the volume and pressure dependences of η from viscosity and density measurements performed only at atmospheric pressure.

Conclusions

Densities of three pentaerythritol ester mixtures, PEB8 + PEC5, PEB8 + PEC7, and PEC5−C9, with a similar viscosity grade, ISO VG32, have been reported in the temperature range from 278.15 K to 353.15 K and at pressures up to 45 MPa. A correction factor due to the viscosity values has been estimated. This factor ranges from $1 \cdot 10^{-4}$ to $5 \cdot 10^{-4}$ g·cm^{-3}. The following order for ρ values, under the same PT conditions has been found: PEC5 > PEC7 > PEC5−C9 > PEB8 + PEC5 > PEB8 + PEC7 > PEB8 > PEC9.

The obtained values for κ_T and α_P are similar for the three PE mixtures. This also includes their behavior with pressure and temperature. The values of the isobaric thermal expansivity are relatively small, decreasing with increasing pressure. For the three mixtures, α_P isotherms present an intersection point in the studied pressure range. The pressure at which α_P is independent of temperature (crossing point) is around 12 MPa for PEC5−C9, around 17 MPa for PEB8 + PEC5, and close to 25 MPa for PEB8 + PEC7. For the binary mixtures PEB8 + PEC5 and PEB8 + PEC7, ρ, κ_T, α_P, and π values are between those of the corresponding pure components. We have found for the three mixtures and four pure PEs that the viscosity is a unique function of TV^{γ} with γ ranging from 3 to 5.4.

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Supporting Information Available:

Additional table reporting the density data without the viscosity correction. This material is available free of charge via the Internet at http://pubs.acs.org.

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