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Experimental Dynamic Viscosities of Dipentaerythritol Ester Lubricants at High Pressure

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In the present work viscosity data for two dipentaerythritol esters (DiPEs) from (303.15 to 373.15) K up to 60 MPa are reported. The experimental measurements were performed with a rotational automated viscometer Anton Paar Stabinger SVM3000 at 0.1 MPa and a rolling-ball viscometer Ruska 1602-830 for high pressures. Modified Vogel−Fulcher−Tammann (VFT) equations are used to represent the temperature and pressure dependence of the viscosity. The viscosity data have been superpositioned as function of the product of the temperature, T, and the volume, V, raised to an exponent γ, namely, the scaling parameter, TV^{γ}. A comparison between the values of this characteristic scaling parameter for the DiPEs with those of other complex esters has been performed.

Introduction

Lubricants are used to facilitate relative motion of solid bodies by minimizing friction and wear between interacting surfaces. In addition to the primary purposes of reducing friction and wear, lubricating oils are also required to carry out a range of other functions, including heat removal, corrosion prevention, transfer of power, providing a liquid seal at moving contacts, and suspension and removal of wear particles.[1,2] One of the most important physical properties of lubricants, which affect the processes of heat and mass transfer, is the dynamic viscosity. The viscosity is also required in many engineering disciplines ranging from the design of transport equipment to the simulation of petroleum reservoirs. The variation of the viscosity with the pressure is especially important for lubricants because, in most mechanical applications, films of fluid are compressed between sliding or rolling surfaces under very high loads. In the elastohydrodynamic regime of lubrication (EHL), the shear viscosity of the lubricant and the pressure-viscosity coefficient, $\alpha = (1/\eta)(\partial\eta/\partial p)_T$, are the main parameters which characterize the film thickness of fluid that protects the mechanical device from high friction and premature wear. The effectiveness of the oil in the rolling element bearings and gears, the energy losses due to viscous dissipation, the improvement of the fatigue life, and reductions in friction and wear are entirely dependent on both properties. Another important characteristic of a lubricant is the viscosity index, VI, which characterizes the temperature dependence of the kinematic viscosity of a lubricant. The higher the value of the VI, the less effect temperature has on the viscosity. In the selection of a lubricant for a given application, the viscosity at the operating temperature is usually the key parameter; nevertheless, if the equipment needs to perform a cold start, changes in the environmental conditions or the machinery need to work under different temperature conditions, so a lubricant which viscosity is less affected for the temperature changes will be favorable. The ideal lubricant would be one whose viscosity is minimally affected by the range of operating temperatures.[2–4]

Polyol esters (POEs) are a type of synthetic lubricants that can be manufactured by reacting a polyalcohol with a mixture of organic acids. The properties of the POE lubricants such as viscosity, density, lubricity, and pour point, among others, can be tuned by selecting different lengths and branching degrees of the acid chain and/or the type of alcohol.[5] They have applications as high-performance lubricants because of their high stability to thermo-oxidation, low volatility, and high flash point.[5–7] The excellent thermal stability of POEs stems from their β-substituted alcohol structure based on trimethylolpropane, pentaerythritol, neopentylglycol, or dipentaerythritol. The esters of these polyhydroxyl alcohols have low volatility, and their bulky structure confers excellent resistance to hydrolysis.[5] In view of these properties, lubricants based on these esters are economical in use and have seen considerable development as synthetic lubricants in automotive applications, marine diesel engines, transmission systems, and the aerospace industry, since several of them perform at medium and high pressures.

Over the last few years, the substitution of traditional refrigerants with alternative fluids caused several important problems that are still not solved. One of them is the identification and development of new suitable lubricants. Although several groups of oils have been proposed, such as polyalkylene glycols (PAGs), POEs, or alkylbenzenes (ABs), their behavior in relation to the various refrigerants and applications is still not well-known. Different studies pointed out that POE lubricants could be primary lubricant candidates for refrigeration systems working with HFCs and carbon dioxide.[8–12] Recent studies[8,12,13] show that carbon dioxide is quite soluble in POE lubricants derived from pentaerythritol, so there is a need of moving toward more viscous ester lubricants. Among the more viscous POEs are those derived of dipentaerythritol, that is, dipentaerythritol esters (DiPEs). The growing demand to save energy and reduce pollution levels has made the design of new lubricants with better efficiency an important area of active research. To get better formulations of POE lubricants, it is important to know the influence of the molecular structure of

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well-defined ester base lubricants in the dependence with pressure and temperature of viscosity and derived properties.

Following our current research projects on environmentally adapted oils, two DiPE lubricants with linear chains, dipentaerythritol hexapentanoate (DiPEC5) and dipentaerythritol hexaheptanoate (DiPEC7), are studied in this work. New dynamic viscosity measurements up to 60 MPa at five temperatures in the range of (303.15 to 373.15) K are reported together with other physical properties that affect the lubrication, such as the VI, the α coefficient, and also the temperature-viscosity coefficient, $\beta = (1/\eta)(\partial\eta/\partial T)_p$.

Experimental Section

Materials. DiPEC5 (CAS Registry No. 76185-96-1, $C_{40}H_{70}O_{13}$) and DiPEC7 (CAS Registry No. 76939-66-7, $C_{52}H_{94}O_{13}$) were provided by Croda-Uniqema (UK). The products were analyzed by ^{1}H, ^{13}C NMR, and mass spectroscopy. The estimated mole fraction purity for both compounds was better than 0.95. Elemental analysis shows that the mass fraction purities of DiPEC5 and DiPEC7 are respectively 0.9998 and 0.999, that is, the major impurities are isomers.

Viscosity Measurements at Atmospheric Pressure. Viscosity at atmospheric pressure was measured with a rotational automated viscometer Anton Paar Stabinger SVM 3000, that allows the measurement of viscosity from (243.15 to 378.15) K and from 0.2 mPa·s to 20 Pa·s. The SVM 3000 Stabinger viscometer is based on a modified Couette principle applied to a tube (outer rotor) filled with a sample liquid that rotates at a constant speed. In this tube is suspended a hollow measuring rotor (titanium rotor). Because of its low density, the measuring rotor is centered in the heavier liquid by buoyancy forces. This rotor is guided axially by a built-in permanent magnet, which induces eddy currents in the surrounding copper casing. The rotor speed adopts an equilibrium between the viscosity-dependent driving torque, which is proportional to the speed difference between the outer tube and the inner rotor, and the retarding torque caused by eddy currents, which is proportional to the inner rotor speed. We have found that the repeatability of this viscometer is better than 0.5 % by performing different sets of measurements of the same substances. The viscosity uncertainty was verified with two reference fluids from Cannon Instrument Comp., S60 and N100, finding that the deviations with the reference data are lower than 1 %. The VI was also determined using the SVM3000 viscometer according to the ASTM D2270 from the kinematic viscosity at (313.15 and 373.15) K.

Viscosity Measurements at High Pressure. The high-pressure viscosity measurements were performed in a rolling-ball viscometer[14–17] (Ruska 1602-830) from (303.15 to 373.15) K and up to 60 MPa. The measurements can be conducted with the unit inclined an angle, θ, of 23°, 45°, and 70° with the horizontal. The angle at which the sphere is rolling and the sphere diameter should be selected taking into account the viscosity range. Thus for higher viscosities, the higher angle and the sphere with the lower diameter should be utilized. Recently[18] a new system to regulate and to measure the temperature in the high-pressure vessel was installed that allows the control of the temperature within 0.1 K over the entire working range. The temperature inside the cellblock was measured with a Pt-100 platinum resistance thermometer and read in the four-wire mode, with an uncertainty of ± 0.02 K. The pressure was measured with two transducers, an HBM PE300 differential pressure gauge and a Druck PMP 4070 absolute pressure gauge that can operate up to (45 and 70) MPa, respectively, both calibrated with an uncertainty of ± 0.02 MPa. More details of the equipment had been published previously.[16,18]

The following procedure was used to perform the viscosity measurements. In the first step, suitable solvents are used to clean the whole system, removing any trace of the previous sample. The system is then evacuated using a vacuum pump. Then, under vacuum, the system is filled with the new sample, and the remaining air (if exists) is purged. Finally, the experimental temperature is fixed. After a minimum wait of four hours until equilibrium conditions are reached and stabilized, the measurements of the rolling times are performed for each pressure, and between each change in pressure we wait for 15 min (minimum) to ensure that the new equilibrium conditions have been reached.

The working equation of this rolling ball viscometer (Ruska 1602-830) relates the dynamic viscosity η as a function of the time, Δt, required for the ball to roll from one end of a fluid-filled tube to the other at a fixed angle, the density difference between the ball and the fluid and the apparatus parameter K. As discussed in a previous article,[18] at a given temperature, the only effects of the pressure are in the geometrical dimensions of the measurement system. By extension the pressure effect on the apparatus parameter K can be considered negligible yielding $K(T,p) \approx K(T)$; thus, we can write:

$$\eta(T, p) = K(T)(\rho_{\text{ball}} - \rho_{\text{fluid}})\Delta t \qquad (1)$$

Then, to determine the calibration function $K(T)$, a given fluid with known density and viscosity at atmospheric pressure under the same temperature conditions considered for viscosity determinations is required. We have selected as a reference fluid the Cannon certified reference standard N100. The rolling time value was taken as the average of six measurements performed at thermal and mechanical equilibrium, its standard uncertainty being lower than 0.2 %. Taking into account the calibration procedure, the rolling time, temperature, and pressure accuracies, as well as the density and viscosity uncertainties of the reference fluid, a final uncertainty of 4 % in the dynamic viscosity measurements has been estimated. To avoid rolling times too long or too short, two balls of different diameter were used as well as three tilt angles of the viscometer tube. The density of both balls is 7.7709 g·cm^{-3}. The densities of the analyzed fluids needed in eq 1 for the dynamic viscosity determination have been measured in our laboratory using a vibrating-tube densimeter over the temperature range from (283.15 to 398.15) K and at pressures up to 70 MPa.[19] We tested the performance of the viscometer by comparing the experimental dynamic viscosity measured for squalane and diisodecyl phthalate (DIDP). For squalane the average absolute deviations (AADs) between our viscosity data[18] at high pressures and those reported by Tomida et al.,[20] Kumagai et al.,[21] Kuss and Golly,[22] Ciotta et al.,[23] and Pensado et al.[17] were (1.2, 1.4, 1.1, 3.2, and 0.8) %, respectively. For DIDP, the AAD between our η values[18] and those published by Al Motari et al.,[24] Harris and Bair[25] (Canberra viscometer), Harris and Bair,[25] (alpha viscometer) and Peleties and Trusler[26,27] were (2.5, 1.1, 3.7, and 1.7) %, respectively. More details of the comparisons are given in a previous article.[18] All of these deviations are in agreement with the estimated uncertainty (4 %) of the Ruska viscometer for the present procedure.

Results and Discussion

In this work the rolling time, Δt, for DiPEC5 and DiPEC7 base lubricants has been measured with the described device up to 60 MPa at five temperatures ranging from (303.15 to 373.15) K. A total of 90 dynamic viscosity points have been obtained from 540 experimental measurements of the rolling

Table 1. Experimental Viscosity, η, of DiPEC5 and DiPEC7 as a Function of Temperature T Obtained with the SVM3000 Rotational Viscometer at $p = 0.1$ MPa

	DiPEC5		DiPEC7	
T/K	run 1 η/mPa·s	run 2 η/mPa·s	run 1 η/mPa·s	run 2 η/mPa·s
283.15	259.0	257.9	260.7	259.1
288.15	189.2	188.5	191.1	190.0
293.15	141.2	140.8	143.1	142.2
298.15	107.6	107.3	109.2	108.5
303.15	83.52	83.31	84.89	84.39
308.15	65.88	65.72	67.04	66.67
313.15	52.73	52.64	53.73	53.45
318.15	42.80	42.75	43.66	43.45
323.15	35.18	35.15	35.93	35.77
328.15	29.24	29.25	29.91	29.79
333.15	24.55	24.59	25.18	25.07
338.15	20.81	20.88	21.39	21.31
343.15	17.79	17.88	18.32	18.27
348.15	15.34	15.44	15.82	15.79
353.15	13.33	13.42	13.77	13.75
358.15	11.66	11.76	12.06	12.06
363.15	10.26	10.36	10.64	10.64
368.15	9.08	9.18	9.44	9.45
373.15	8.09	8.18	8.42	8.43

Table 2. Experimental Viscosity, η, of DiPEC5 and DiPEC7 Measured with the High-Pressure Rolling Ball Viscometer as a Function of Temperature T and Pressure p

	T/K				
p/MPa	303.15	313.15	333.15	353.15	373.15
			DiPEC5		
0.1	85.9	54.3	25.0	13.5	8.22
1	87.2	55.1	25.4	13.6	8.32
5	93.2	58.8	26.9	14.4	8.78
10	101	63.6	29.0	15.45	9.38
20	119	74.4	33.6	17.7	10.6
30	139	86.6	38.6	20.1	12.0
40	163	100	44.2	22.8	13.5
50	189	116	50.3	25.7	15.2
60	219	133	56.9	28.8	16.9
			DiPEC7		
0.1	86.3	55.8	25.5	13.8	8.46
1	87.7	56.6	25.9	14.0	8.56
5	93.9	60.3	27.5	14.8	9.04
10	102	65.3	29.6	15.9	9.66
20	121	76.3	34.3	18.2	11.0
30	142	88.9	39.5	20.8	12.4
40	167	103	45.3	23.6	14.0
50	194	119	51.7	26.6	15.7
60	226	138	58.8	30.0	17.5

time. The viscosity values of DiPEC5 and DiPEC7 measured in the temperature range from (283.15 to 373.15) K at atmospheric pressure with the rotational Anton-Paar SVM3000 viscometer are presented in Table 1. Two sets of viscosity values for each DiPE at atmospheric pressure were performed finding AADs between them around 0.4 %. In Table 2, the values measured at high pressure with the rolling ball viscometer are given. The experimental values measured with the Ruska viscometer agree with those measured with the SVM3000 viscometer at atmospheric pressure with AADs of 2 % and 1 % for DiPEC5 and DiPEC7, respectively.

In the present work we have fitted the η values of Table 1 obtained from the Stabinger viscometer to the Vogel−Fulcher−Tammann (VFT) correlation given by:

$$\eta(T) = A \exp\left(\frac{B}{T - C}\right) \tag{2}$$

Pensado et al.[28] used eq 2 to estimate the glass transition temperatures T_g, at atmospheric pressure of three pentaerythritol esters (PEs), finding a very good agreement with T_g data measured by differential scanning calorimetry (DSC). Following the same procedure in this work, we have estimated the T_g values for both DiPEs obtaining (183.9 and 184.4) K for DiPEC5 and DiPEC7, respectively. Unfortunately, we have not found in the literature any other experimental or predicted T_g value for these compounds.

Glass is a microscopically disordered solid form of matter that results when a fluid is cooled or compressed in such a manner that it does not crystallize. Almost all types of materials are capable of glass formation, including polymers, ionic and van der Waals liquids, metal alloys, and molten salts. Given such diversity, general principles by which different glass-forming materials can be systematically classified are invaluable. One such principle is the classification of glass formers according to their fragility.[29] Fragility measures the rapidity with which a liquid's properties (such as viscosity) change as the glass state is approached. This fragility is not the familiar mechanical fragility of a glass, but the fragility of molecular architecture in the glass-forming melt.[30] Thus, fragile glass-forming liquids are supercooled liquids where the increase of relaxation time τ with decreasing temperature T is more rapid than that of the Arrhenius law ($C = 0$ in eq 2). While strong liquids (low C) follow Arrhenius temperature dependence of transport properties, the fragile liquids exhibit strongly non-Arrhenius behavior (high C). The Angell strength parameter D (B/C from VFT correlation) accounts for this departure of $\eta(T)$ from the Arrhenius behavior ($C = 0$) and is widely used in this classification. The parameter D is large (small values of C) for "strong" liquids where the viscosity approaches Arrhenius temperature dependence and is small (high values of C) for "fragile" liquids.[31,32] Typical values[33,34] for the strength parameter D have been found to range from 2.7 for 2-ethylhexyl benzoate (very fragile) to 161 for SiO_2 (very strong). Glycerol ($D = 18$ at 0.1 MPa) is often considered as a moderately strong liquid or a moderate fragile one at atmospheric pressure.[35,36]

From the above VFT correlation we have obtained D values of 6.9 for DiPEC5 and 6.7 for DiPEC7. For pentaerythritol tetra-2-ethylhexanoate (PEB8), pentaerythritol tetrapentanoate (PEC5), pentaerythritol tetraheptanoate (PEC7), and pentaerythritol tetranonanoate (PEC9) using the values of the parameters B and C of the VFT correlation determined by Pensado et al.[37] the Angell strength parameter takes values of 5.2, 4.7, 4.6, and 5.8. Hence, the above PEs and DiPEs are quite fragile (i.e., do not follow Arrhenius behavior), with the DiPE being slightly less fragile than PE and also than other complex esters such as 2-ethylhexyl benzoate, bis(2-ethylhexyl)phthalate, and squalane with D values of 2.75 and 4.76, respectively.

Concerning the high-pressure viscosity measurements, in Figure 1 the dynamic viscosity is plotted against the temperature at different pressures for DiPEC5 and DiPEC7. As can be seen in this figure (and in Tables 1 and 2), the dynamic viscosity of both fluids is quite similar and also their temperature and pressure dependencies. The viscosity increases slightly with the increase of the acid chain length of the DiPE, but this fact is more important in other POEs, as PEs.[15] In Figure 2 the dynamic viscosities of the two tested fluids are plotted against pressure at 303.15 K, together with the η values for four PEs, PEB8, PEC5, PEC7, and PEC9, previously measured[15,17] in our laboratory. The viscosity of POEs increases with the length of the side chains but the rate at which it changes varies with the type of polyalcohol, this being more marked for esters derived of pentaerythritol than for the corresponding ones derived from dipentaerythritol. Previous studies[5,6,38] on ester lubricants conclude that the viscosity can be enhanced by increasing the branching degree, the acid chain length

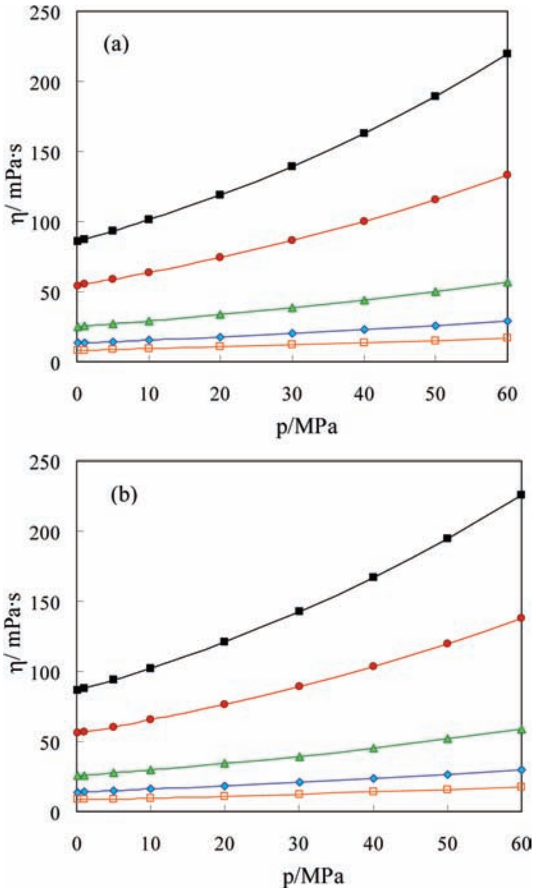

Figure 1. Experimental dynamic viscosity against pressure at different temperatures. (a) DiPEC5, (b) DiPEC7: ■, 303.15 K; ●, 313.15 K; ▲, 333.15 K; ◆, 353.15 K; □, 373.15 K.

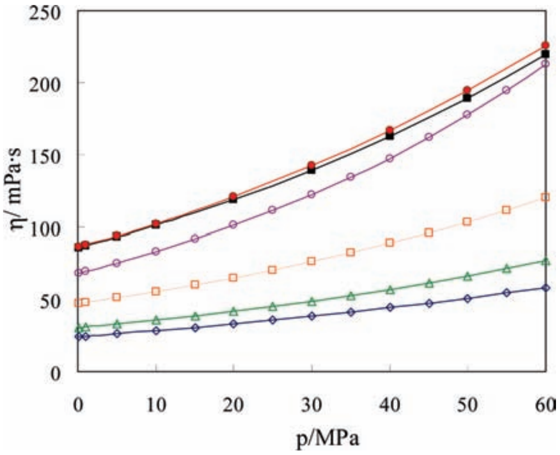

Figure 2. Experimental dynamic viscosity against pressure at $T = 303.15$ K for different polyolester lubricants. ■, DiPEC5; ●, DiPEC7; ◇, PEC5; △, PEC7; □, PEC9; ○, PEB8.

of the molecule, or the molecular weight. The obtained results show that an increase in the functionality of the polyalcohol leads to an increase of the viscosity, but then, the effect of modifying the length of the side chains is minor. This effect is due to the increase of the number of the polar ester groups, and consequently, the number of dipole−dipole interactions among the POE molecules is higher. We have found in a previous article[19] that the density of DiPEs is higher than that of corresponding PEs.

The experimental viscosity data for each fluid measured with the Ruska apparatus were correlated as functions of temperature and pressure with the following modification of the VFT equation, proposed by Comuñas et al.[39]

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

where

$$E = E_0 + E_1 T + E_2 T^2 \tag{4}$$

We have selected as a reference pressure $p_{\mathrm{ref}} = 0.1$ MPa. The parameters A, B, and C have been determined in a preliminary fit of the viscosity as a function of the temperature at the reference pressure of 0.1 MPa, and coefficients F, E_0, E_1, and E_2 have been fitted to the viscosity measurements at pressures different from the reference pressure using the Levenberg−Marquardt[40] algorithm. In this equation, $C = T_0$, $B = T_0 D$, and the Angell strength parameter D are pressure-independent, whereas the pre-exponential factor is pressure- and temperature-dependent. Nevertheless, in the case of the structural relaxation times with VFT it has been observed at moderate pressures ($P < 400$ MPa) that the Vogel temperature T_0 always increases with pressure,[35,41–45] whereas the strength parameter D seems to be pressure-independent for some authors,[46,47] but it is considered pressure-dependent for other authors.[48,49] Considering these previous literature results, in the present work to correlate the viscosities at high pressures another two modifications of the VFT equation[50,51] were used

$$\eta = \exp(a' + b'p + (c' + d'p + e'p^2)/(T - T_0)) \tag{5}$$

$$\eta = \exp(a'' + b''p + DT_0(p)/(T - T_0(p))) \tag{6}$$

where

$$T_0(p) = x + yp + zp^2 \tag{7}$$

In eq 5 the Angell strength parameter D is pressure-dependent, $D = (c' + d'p + e'p^2)/T_0$, whereas in eq 6, D is constant. The values of the parameters of eqs 3 and 4 as well as the parameters obtained for eqs 5 to 7 are given in Table 3. The AADs are similar for eqs 5 and 6 and slightly lower for those obtained with eq 3. Figures 3 and 4 show how both D and T_0 (from eq

Table 3. Parameters of Equations 3 to 7 and AAD

	DiPEC5	DiPEC7
	eqs 3 to 4	
A/mPa·s	0.06027	0.05308
B/K	1062.55524	1124.81222
C/K	156.88204	151.16709
F	4.40018	4.83080
E_0/MPa	−360.93395	−799.36345
E_1/MPa·K^{-1}	2.73872	5.38070
E_2/MPa·K^{-2}	−0.00235	−0.00607
AAD/%	0.41	0.56
σ	0.41	0.54
	eq 5	
a'	−2.81803	−2.78416
b'	0.00444	0.00408
c'	1067.84111	1071.87490
d'	1.88149	1.98560
e'	−0.00395	−0.00381
T_0	156.25299	155.23456
AAD/%	0.36	0.53
σ	0.34	0.51
	eqs 6 to 7	
a''	−2.89326	−2.87418
b''	0.007400	0.007253
D	7.11497	7.23856
x	153.96508	152.59198
y	0.10213	0.10555
z	−0.000326	−0.000310
AAD/%	0.39	0.55
σ	0.38	0.53

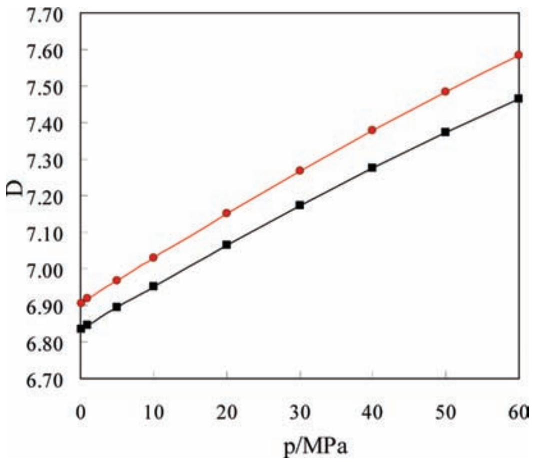

Figure 3. Pressure dependence of the Angell parameter from eq 5, i.e., $D = (c' + d'p + e'p^2)/T_0$ for ■, DiPEC5 and ●, DiPEC7.

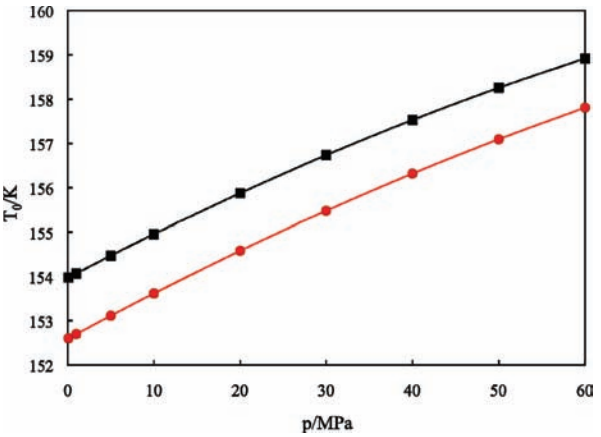

Figure 4. Pressure dependence of T_0 of eq 7 for ■, DiPEC5 and ●, DiPEC7.

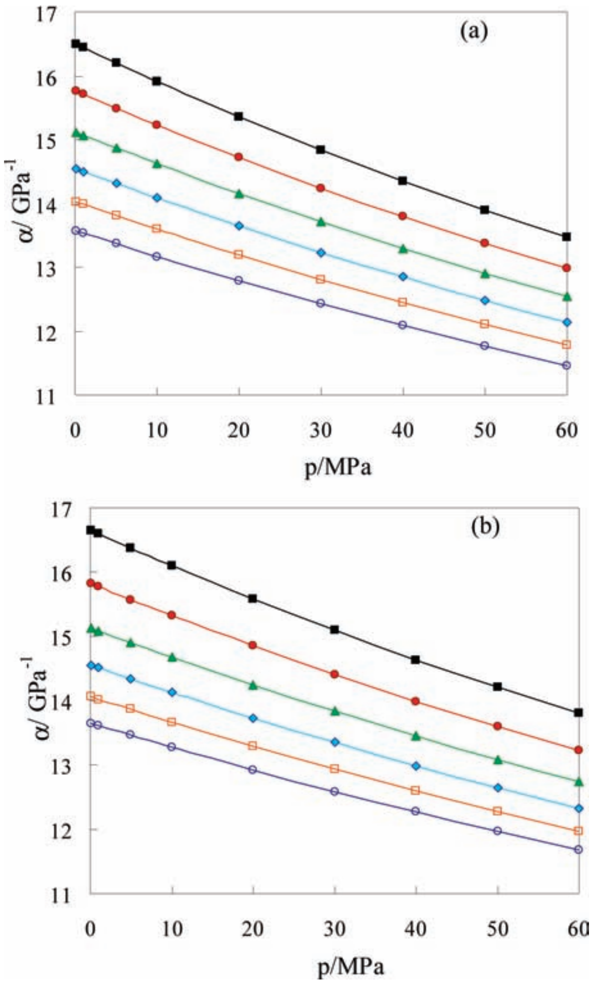

Figure 5. Plots of the pressure−viscosity coefficient versus pressure determined from eq 8 at different temperatures for (a) DiPEC5 and (b) DiPEC7. ■, 313.15 K; ●, 323.15 K; ▲, 333.15 K; ◆, 343.15 K; □, 353.15 K; ○, 363.15 K.

6) increase with the pressure. A similar behavior was found by Harris and co-workers for six ionic liquids.[49–52]

In the EHL, the shear viscosity of the lubricant and the pressure−viscosity coefficient, α, are the main parameters which characterize the film thickness of fluid that protects the mechanical device from high friction and premature wear. Several authors[53,54] indicate that fluids of a higher α value produce thicker lubricant films, so rolling-element bearings, gears, and rotors are better protected at high pressures. Thus, according to Errichello,[54] an increase of 16 % in the film thickness increases the bearing life more than four times.[55–57]

The α coefficient could be measured either directly by assessing viscosity as a function of pressure using a high-pressure apparatus or indirectly by measuring film thickness in an optical interferometer. Nevertheless, there is controversy over the validity of these relations that relate the pressure−viscosity coefficient and the film thickness, and the appropriate definition of the α parameter.[58,59] Likely for these reasons among others α values obtained using the direct and indirect approaches can show large discrepancies. One of the definitions to extract the pressure−viscosity coefficient from experimental viscosity values is due to Dowson and Higginson[60] who defined the coefficient α as:

$$\alpha(p) = \frac{1}{\eta}\left(\frac{\partial \eta}{\partial p}\right)_T \tag{8}$$

This definition of the pressure−viscosity coefficient takes into account the local variation of the slope of the log η versus pressure curves. This definition is similar to that usually used for the isothermal compressibility in the case of density. The pressure−viscosity coefficient obtained from eq 8 has been plotted against pressure at different temperatures for the studied lubricants in Figure 5. The pressure−viscosity coefficients for DiPEC5 and DiPEC7 decrease when the pressure or the temperature increases. The values of the α coefficient for the DiPE with longer side chains are slightly higher. Randles[5] remarked that the α values of ester lubricants increases with the length of the side chains of the molecules and the degree of branching. These observations seem to be in agreement with the results found in the present work. A similar trend was found for PEC5, PEC7, PEC9, and PEB8.[15,17] The α values of DiPEC5 and DiPEC7 are higher than those of PEC5 and PEC7.

Another important quantity to characterize a lubricant is the temperature−viscosity coefficient. This coefficient is defined by the following expression:

$$\beta = -\frac{1}{\eta}\left(\frac{\partial \eta}{\partial T}\right)_p \tag{9}$$

In Figure 6 we present the temperature−viscosity coefficient for the two ester lubricants. This coefficient decreases when the temperature rises, whereas the dependence with pressure is very smooth. Again, the differences between the two lubricants are quite small, the values for DiPEC7 being slightly lower. The increase of β with the length of the side chains is in agreement with previous results for PE lubricants.[15,17]

Besides, the VI characterizes the temperature dependence of the lubricant's kinematic viscosity. Thus, a higher VI involves

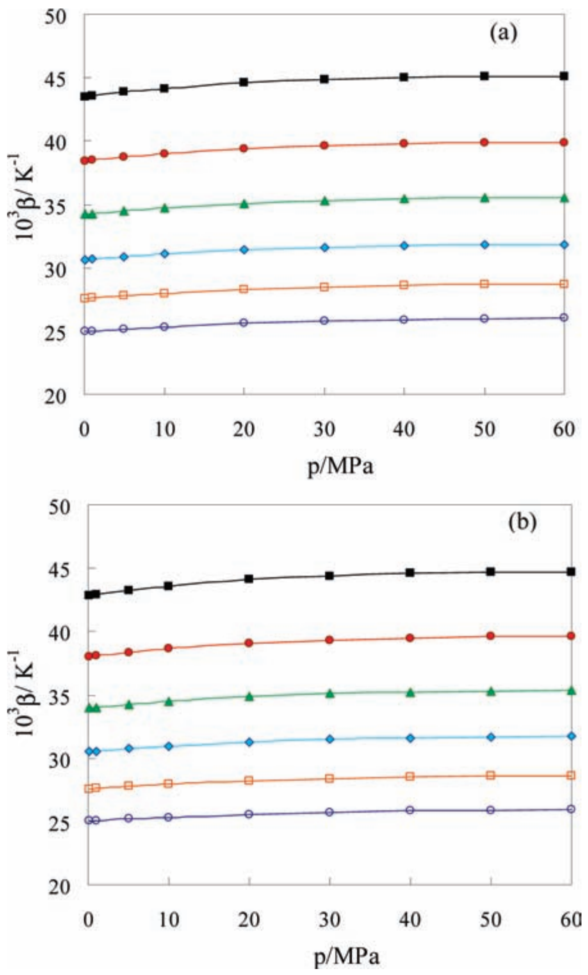

Figure 6. Plots of the temperature−viscosity coefficient versus pressure at different temperatures for (a) DiPEC5 and (b) DiPEC7. ■, 313.15 K; ●, 323.15 K; ▲, 333.15 K; ◆, 343.15 K; □, 353.15 K; ○, 363.15 K.

a smaller relative change in viscosity with temperature. The values obtained for the fluids studied in this work using the SVM 3000 Stabinger viscometer are VI = 138 for DiPEC5 and VI = 145 for DiPEC7, in agreement with the fact that temperature−viscosity coefficients for DiPEC7 are lower than for DiPEC5. These values are higher than those corresponding to the PEs with the same type and size of side chains.

Roland and Casalini and co-workers,[61–64] among others,[28,33,65–67] have shown the superposition of viscosity[62] for various glass-forming liquids, lubricants, ionic liquids, and polymers when expressed as a function of the product TV^{γ}; that is, η is a unique function of TV^{γ}

$$\eta(T, V) = \eta(T, p) = f(TV^{\gamma}) \qquad (10)$$

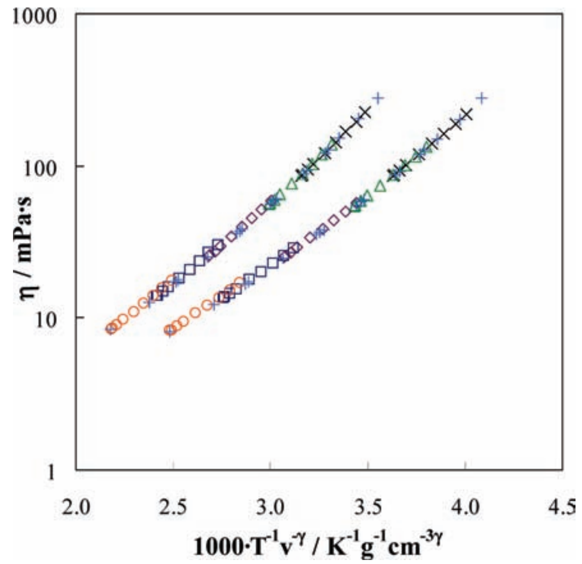

Figure 7. Superpositioned viscosities of DiPEC5 and DiPEC7. Symbols represent the different isotherms: ×, 303.15 K; △, 313.15 K; ◇, 333.15 K; □, 353.15 K; ○, 373.15 K, +, 0.1 MPa. The pressure ranges from ambient to 60 MPa.

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,[62,68] because it reflects the magnitude of the intermolecular forces and also the contribution from internal molecular modes, such as vibrations and torsions. In addition, the exponent γ links the thermodynamic and the transport behavior.[62] We have determined in a previous work[66] the exponent γ (eq 10) for pure PEs (PEC5, PEC7, PEC9, and PEB8) and for a number of molecular and ionic liquids elsewhere.[28] Like in the previous article,[66] in this work, for each DiPE, the viscosity data collapsed onto a single master curve when plotted as a function of TV^{γ} (Figure 7), for a given γ value. To obtain γ more precisely, we tried values stepped by 0.1 and fitted different functionalities to the experimental data. The best regression coefficients were obtained using polynomial functions obtaining for DiPEC5, $\gamma = 3.2$, and for DiPEC7, $\gamma = 3.1$. The trend found for the scaling exponent γ for the POEs studied by us is then PEC7 ($\gamma = 5.4$) > PEC5 ($\gamma = 5.3$) > PEC9 ($\gamma = 4.5$) > PEB8 ($\gamma = 3.6$) > DiPEC5 ($\gamma = 3.2$) > DiPEC7 ($\gamma = 3.1$). These exponents are lower than the values for the van der Waals liquids with low molecular weight,[28] in agreement with the fact that PEs and DIPEs are more polar and branched. The scaling parameter for POE compounds is higher than those of hydrogen-bonded liquids and most of the ionic liquids.[28] The fact that γ values for DiPE are lower than that of PE is likely due to the increase of bonds and of the number of polar groups. This behavior was previously found for other compounds such as PAG dimethyl ethers.[28] The γ values of both DiPEs are quite similar to those previously published[33] for other types of ester lubricants, dibutylphthalate ($\gamma = 3.2$), bis(2-ethylhexyl)phthalate ($\gamma = 3.65$), DIDP ($\gamma = 3.96$), and 2-ethylhexylbenzoate ($\gamma = 3.69$).

Conclusions

New viscosity data are reported for two DiPEs, DiPEC5 and DiPEC7. The viscosity determinations have been performed with an estimated uncertainty better than 4 % over the whole viscosity range in the temperature interval from (303.15 to 373.15) K and up to 60 MPa. The viscosity, pressure, and temperature coefficients and the VI were analyzed for the tested fluids. In the case of viscosity, the VI, and α coefficient, the following sequences have been found: η(DiPEC7) > η(DiPEC5), VI(DiPEC7) > VI(DiPEC5), and α(DiPEC7) > α(DiPEC5), whereas the opposite trend is obtained for the temperature viscosity coefficient and the scaling parameter, β(DiPEC7) < β(DiPEC5) and γ(DiPEC7) < γ(DiPEC5).

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