4088 *J. Chem. Eng. Data* **2010,** *55,* 4088–4094

How Pressure Affects the Dynamic Viscosities of Two Poly(propylene glycol) Dimethyl Ether Lubricants

Xavier Paredes, Alfonso S. Pensado, María J. P. Comuñas, and Josefa Fernández*

Laboratorio de Propiedades Termofísicas, Departamento de Física Aplicada, Universidade de Santiago de Compostela,
E-15782 Santiago de Compostela, Spain

The dynamic viscosity of two poly(propylene oxide) dimethyl ethers with average molecular weights higher than 1.3 $\text{kg}\cdot\text{mol}^{-1}$ are the object of study in this work. The experimental measurements have been performed with a rotational automated viscometer and a high-pressure rolling-ball viscometer up to 60 MPa at five temperatures ranging from (303.15 to 373.15) K. We present other physical properties that affect the lubrication, such as the viscosity index, the pressure−viscosity coefficient, and the temperature−viscosity coefficient. Several Vogel−Fulcher−Tammann (VFT) type equations were used to fit the viscosity experimental values to the pressure and temperature. The viscosity data have also been fitted as a function of temperature and volume to the thermodynamic scaling model of Roland et al.

Introduction

Polyalkylene glycol ethers (PAGs) are the largest single class of synthetic lubricant bases. They can be used as automotive antifreeze, brake fluid, water-based hydraulic fluids, hydrocarbon gas compressors, textile lubes, metalworking fluid, food grade lubricants, and high-temperature bearing and gear lubricants.[1,2] Besides, different studies pointed out that PAG oils could be primary lubricant candidate for refrigeration systems working with hydrofluorocarbons (HFCs) and CO_2.[3,4] PAGs are prepared by the reaction of epoxides, usually ethylene and propylene oxide (EO and PO), with compounds that contain active hydrogen in the presence of a basic catalyst. Variation of the ratio of the epoxides and the end groups leads to different products. The molecular weight and viscosity of PAGs can be significantly influenced during production and can be adjusted within narrow limits.[5] The possibility of engineering products in this way distinguishes them from many other lubricants. Polyalkylene ethers are also known plasticizers for low melting polyesters such as poly(butylene terephthalate) and poly(ethylene terephthalate).

One of the main advantages[1,2] of PAGs is that these lubricants decompose completely into volatile compounds under high-temperature oxidizing conditions. This results in low sludge build up under moderate-to-high operating temperatures or complete decomposition without leaving deposits in certain extremely hot applications. PAG miscibility with water increases with the number of EO units. The hygroscopic character of the PAGs is dependent on their hydroxyl group content; it decreases with increasing molecular weight and the number of ether bonds. The solubility in water decreases in the same way. Even if the PAG fluid does not initially contain any water, it has the tendency to absorb moisture from the atmosphere.

Lubricants are materials used to facilitate the relative motion of solid bodies by minimizing friction and wear between interacting surfaces. The viscous behavior of a lubricant as a function of temperature, pressure, and shear rate is crucial in determining its ability to form a layer of oil between rolling surfaces to reduce friction and wear. The pressure−viscosity coefficient, α, quantifies the film-generating capability of a lubricant in tribological contacts, at isothermal conditions.[6,7] This coefficient is very dependent on the chemical structure of the base oil[6,8,9] and could be modified using small quantities of additives. The viscosity index (VI) is another important parameter in lubrication design because it quantifies the temperature dependence of the lubricant viscosity.

Kinematic viscosities for PAG lubricants at atmospheric pressure usually range from (8 to 100 000) $\text{mm}^2\cdot\text{s}^{-1}$ at 313.15 K, and the VI of PAGs can reach values around 200 for low-molecular-weight PAGs and 430[2,5] for high-molecular-weight PAGs. The viscosity dependence on pressure under isothermal conditions for PAGs shows a lack of experimental values. Following our current research projects on environmentally adapted oils, two double end-capped PO PAGs with average molecular weights higher than 1.3 $\text{kg}\cdot\text{mol}^{-1}$ are the object of study in this work. New dynamic viscosity measurements up to 60 MPa at five temperatures ranging from (303.15 to 373.15) K are reported together with other physical properties that affect the lubrication, such as the VI value, the α value, and the temperature−viscosity coefficient, β.

Experimental Section

Materials. The two double end-capped poly(propylene glycols), $CH_3O[CH_2CH(CH_3)O]_mCH_3$, were provided by Croda. The samples are aliquots of those used by Fandiño et al.[10] The molecular masses of the PAGs were determined with matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry.[11] PAG1 has a weight average molecular mass, M_w, of 1.385 $\text{kg}\cdot\text{mol}^{-1}$, and that of PAG2 is 1.717 $\text{kg}\cdot\text{mol}^{-1}$, the estimated uncertainties being lower than $1\cdot10^{-3}$ $\text{kg}\cdot\text{mol}^{-1}$. The polydispersity indexes were respectively 1.017 and 1.022, so both PAGs can be considered as monodisperse. The number of PO units, $[CH_2CH(CH_3)O]$, is $m = 23$ for PAG1 and $m = 29$ for PAG2.[10] The samples were degassed and dried by keeping them under vacuum (approximately 1 Pa) for (8 to 15) h, at a temperature above 303 K.

---

* Corresponding author. Tel.: 34-881814046; fax: 34-981520676. E-mail: josefa.fernandez@usc.es.

10.1021/je100285a

Measurement Techniques. The viscosity at atmospheric pressure was measured with a rotational automated viscometer Anton Paar Stabinger SVM3000. This apparatus allows, according to the manufacturer, density, dynamic viscosity, and kinematic viscosity measurements over the range (253.15 to 373.15) K of fluids with dynamic viscosities from 0.2 mPa·s to 20 Pa·s. The VI was determined using the SVM3000 viscometer according to the ASTM D2270 from the kinematic viscosity at (313.15 and 373.15) K. The reproducibility of the dynamic viscosity and density measurements with this technique is 0.35 % and 0.5 $\text{kg}\cdot\text{m}^{-3}$, respectively. We have verified the viscosity uncertainty with two reference fluids from Cannon Instrument Comp., S60 and N100, finding that the deviations are lower than 1 %.

The high-pressure viscosity measurements were performed in a rolling-ball viscometer[12−16] (Ruska 1602-830) from (303.15 to 373.15) K and up to 60 MPa. The measurements can be conducted with the unit inclined at different angles with the horizontal. The angle and the sphere diameter would vary to take the viscosity range into account. Thus, the higher the viscosity, the quicker the setting (higher angle and sphere of smaller diameter) should be used. Several elements of the apparatus were recently modified by Paredes et al.[16] from the original device.[14] The temperature inside the cellblock was measured with an uncertainty of ± 0.02 K. The pressure was measured with two transducers, both calibrated with an uncertainty of ± 0.02 MPa, a HBM PE300 differential pressure gauge and a Druck PMP 4070 absolute pressure gauge that can operate up to (45 and 70) MPa, respectively. The procedure used to perform the measurements has been explained in previous articles.[16,17]

Working Equation. For the rolling-ball viscometer geometry, the dynamic viscosity η is a function of Δt, the time required for the ball to roll from one end of a fluid-filled tube to the other at a fixed angle, of the density difference between the ball and the fluid and of the apparatus parameter K, according to the following equation:[16,17]

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

The determination of the calibration function $K(T)$ was explained in detail in previous articles.[16,17] To optimize the rolling times, two balls and different tilt angles were used. Considering the calibration procedure, temperature, pressure, and falling-time accuracies and the density and viscosity uncertainties of the reference fluid (Cannon certified reference standard N100), we have estimated[16,17] a final expanded uncertainty of less than ± 4 % in the present dynamic viscosity measurements.[16] The instrument performance was tested[16] by comparing the experimental dynamic viscosity measured for diisodecyl phthalate (DIDP) and squalane. For DIDP, the maximum average absolute deviation (AAD) between our η values and those found in the literature was 3.7 %, and for squalane the maximum AAD between our viscosity data at high pressures and those found in the literature was 3.2 %. More details of the comparisons are given in a previous article.[16] All of these deviations are in agreement with our estimated uncertainty for our viscosity measurements (4 %).

Results and Discussion

The rolling times for the two PAG base lubricants have been measured with the Ruska rolling ball device up to 60 MPa at five temperatures ranging from (303.15 to 373.15) K. The rolling time value, Δt, was taken as the average of six measurements performed at thermal and mechanical equilibrium, its standard uncertainty being lower than 0.2 %. The densities of the analyzed fluids needed in eq 1 for the dynamic viscosity determination have been taken from a recent work of Fandiño et al.[18] We have also measured the viscosities of the two PAGs in the temperature range from (278.15 to 373.15) K, at atmospheric pressure with a rotational Anton Paar SVM3000 viscometer. These values are presented in Table 1, whereas in Table 2, the values obtained with the rolling-ball viscometer are given. The experimental values measured with the high-pressure device agree with those measured with the SVM3000 viscometer at atmospheric pressure with AADs of 1.8 % and 0.6 % for PAG1 and PAG2, respectively. The trends of the viscosity with temperature and pressure can be observed in Figure 1. The viscosity increases with the average molecular mass of the PAG. The same trend was found[10] for the density and internal pressure, whereas for the compressibility and the isobaric thermal expansivity the opposite tendency is found.

Table 1. Experimental Viscosity, η (mPa·s), of PAG1 and PAG2 at Different Temperatures and Atmospheric Pressure Measured with the SVM3000 Viscometer

T/K	η_{PAG1}/mPa·s	η_{PAG2}/mPa·s
278.15	243.1	351.6
283.15	177.1	253.0
288.15	133.0	188.2
293.15	102.3	143.6
298.15	80.28	111.8
303.15	64.24	88.89
308.15	52.28	71.86
313.15	43.19	58.99
318.15	36.17	49.10
323.15	30.65	41.39
328.15	26.26	35.29
333.15	22.71	30.39
338.15	19.82	26.41
343.15	17.43	23.14
348.15	15.44	20.42
353.15	13.76	18.14
358.15	12.34	16.23
363.15	11.13	14.59
368.15	10.09	13.19
373.15	9.185	11.98

Table 2. Experimental Viscosity, η (mPa·s), of PAG1 and PAG2 at Different Temperatures and Pressures Measured with the High-Pressure Rolling-Ball Viscometer

	T/K				
p/MPa	303.15	313.15	333.15	353.15	373.15
			PAG1		
0.1	65.0	43.8	22.2	13.3	9.11
1	66.1	44.5	22.6	13.5	9.22
5	71.2	47.6	24.0	14.2	9.76
10	78.0	51.8	25.9	15.3	10.5
20	93.4	61.1	30.1	17.5	11.9
30	112	72.0	34.8	20.0	13.6
40	133	84.5	40.1	22.7	15.3
50	158	99.0	46.1	25.7	17.1
60	187	116	52.7	28.9	19.1
			PAG2		
0.1	89.2	59.8	30.6	18.1	12.0
1	90.7	60.7	31.0	18.3	12.1
5	97.8	65.2	33.0	19.4	12.8
10	108	71.1	35.7	20.9	13.7
20	129	84.5	41.6	24.1	15.6
30	155	99.9	48.3	27.6	17.8
40	186	118	55.9	31.5	20.1
50	222	139	64.4	35.7	22.5
60	264	162	74.0	40.3	25.2

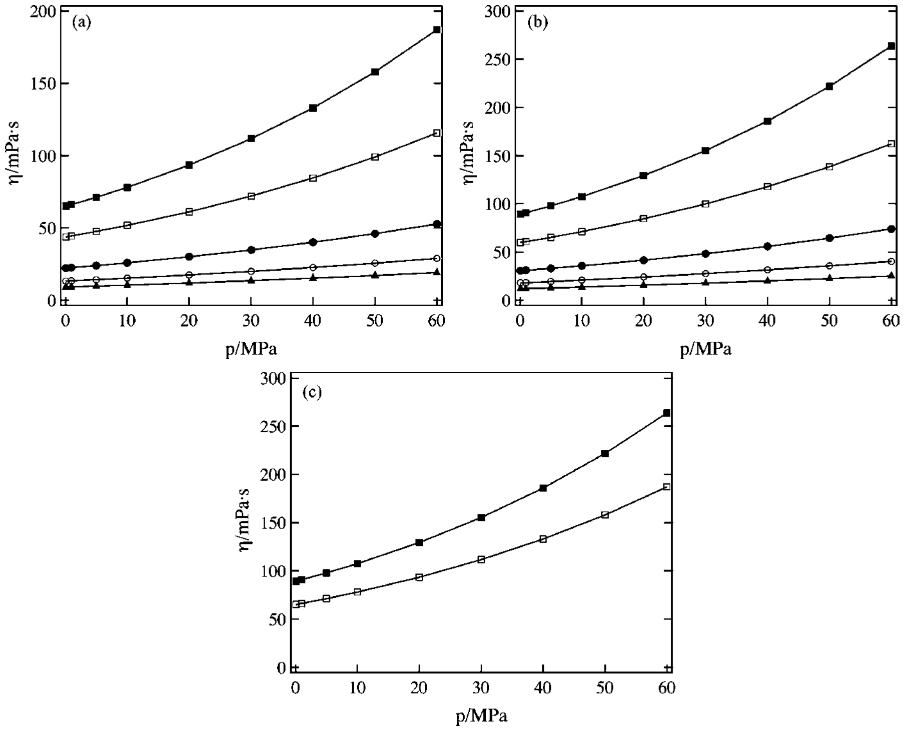

Figure 1. Dynamic viscosity as a function of temperature and pressure for (a) PAG1, (b) PAG2: ■, 303.15 K; □, 313.15 K; ●, 333.15 K; ○, 353.15 K; ▲, 373.15 K. (c) Dynamic viscosity as a function of the pressure at 303.15 K: ■, PAG1; □, PAG2.

Table 3. Parameters of Equations 2 to 6 and AADs

	PAG1	PAG2
	eq 2	
A/mPa·s	0.32506	0.25111
B/K	623.47896	788.13434
C/K	185.64455	169.00719
F	6.53648	6.42802
E_0/MPa	−2248.5847	−1485.95806
E_1/MPa·K^{-1}	13.79361	9.10318
E_2/MPa·K^{-2}	−0.01729	−0.01028
AAD/%	0.96	0.35
σ/mPa·s	0.66	0.46
	eq 4	
a'	−0.91163	−1.18128
b'	0.00396	0.00218
c'	564.45999	725.58595
d'	1.63735	2.19267
e'	−0.00234	−0.00303
T_0	192.30742	175.25588
AAD/%	0.97	0.39
σ/mPa·s	0.56	0.50
	eq 5	
a''	−0.99178	−1.29122
b''	0.00783	0.00656
D'	3.10164	4.44186
x	189.49552	171.43500
y	0.15003	0.16376
z	−0.0004248	−0.0004293
AAD/%	0.93	0.32
σ/mPa·s	0.32	0.12

We have used a modification of the Vogel−Fulcher−Tammann (VFT) equation proposed by Comuñas et al.[19] to correlate the experimental viscosity data obtained with the high-pressure device for each fluid as a function of temperature and pressure:

$$\eta(p,T) = A\left(\frac{p+E}{p_{\mathrm{ref}}+E}\right)^{F}\exp\left(\frac{B}{T-C}\right) \tag{2}$$

where

$$E = E_0 + E_1T + E_2T^2 \tag{3}$$

We have selected as the 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, 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[20] algorithm. The values of the parameters of eqs 2 and 3 are given in Table 3. The experimental points for each fluid fall within a narrow range well-centered with respect to the corresponding equation, yielding an AAD of at worse 1 % which is a measure of the dispersion of the data. In eq 2, the three parameters $C = T_0$, $B = T_0D$, 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,[21−26] whereas the strength parameter D seems to be pressure-independent for some authors,[27,28] but it is considered pressure-dependent for others.[29,30] Considering these previous literature results, in the present work we correlate the viscosities at high pressures with other two modifications of the VFT equation:[31,32]

$$\eta = \exp(a' + b'p + (c' + d'p + e'p^2)/(T - T_0)) \tag{4}$$

$$\eta = \exp(a'' + b''p + DT_0(p)/(T - T_0(p))) \tag{5}$$

where

$$T_0(p) = x + yp + zp^2 \tag{6}$$

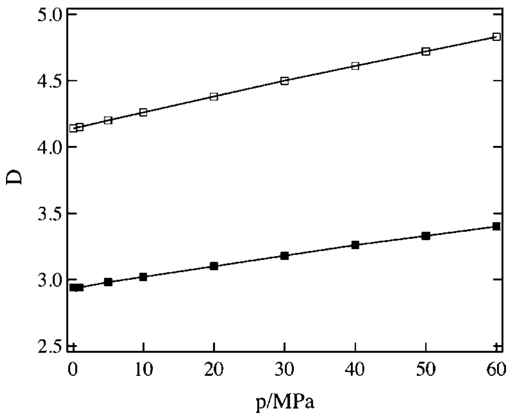

Figure 2. Pressure dependence of the Angell parameter of eq 4, $D = (c' + d'p + e'p^2)/T_0$, for ■, PAG1; □, PAG2.

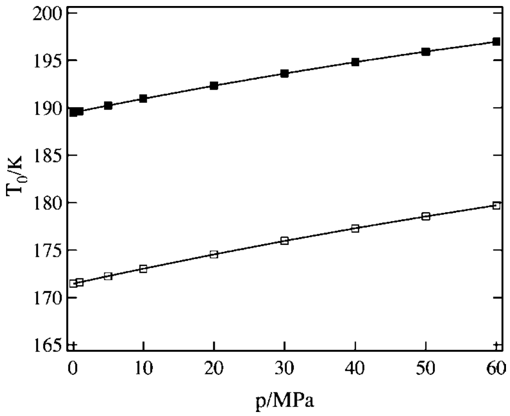

Figure 3. Pressure dependence of T_0 of eq 6 for ■, PAG1; □, PAG2.

The Angell strength parameter in eq 4 is pressure-dependent obeying the relation $D = (c' + d'p + e'p^2)/T_0$, whereas in eq 5, D is constant. The values of the parameters of eqs 4, 5, and 6 are given in Table 3. The AADs are similar for eqs 4 and 5 and slightly higher to those obtained with eq 2. Figures 2 and 3 show respectively how both D and T_0 (from eq 5) increase with the pressure. It is possible to observe similar behavior for dipentaerythritol esters[17] and for ionic liquids.[30−33]

We have used the original VFT equation to estimate the glass transition temperatures T_g at atmospheric pressure of the two compounds, obtaining (194.2 and 196.3) K for PAG1 and PAG2, respectively. Mattson et al.[34] have determined the glass transition temperatures using dielectric spectroscopy of the series $CH_3O[CH_2CH(CH_3)O]_mCH_3$ with $m = 1, 2, 3, 7, 17$, and 34. According to Figure 3 of this article,[34] the glass transition temperatures corresponding to the weight average molecular mass of the two PAGs studied in this work are around (192 and 195) K for PAG1 ($m = 23$) and PAG2 ($m = 29$), respectively, in good agreement with our estimated T_g values.

When the moving parts of a mechanical device are working in the elastohydrodynamic regime of lubrication (EHL), the main parameters characterizing the film thickness of the fluid in the contact points protecting them from high friction and premature wear are the shear viscosity and the pressure−viscosity coefficient, α, of the fluid. According to several authors,[7,35] fluids of higher α value produce thicker lubricant films, providing then a better protection at high pressures for rolling-element bearings, gears, and rotors. Errichello[7] has indicated that an increase of 16 % in the film thickness increases the bearing life more than four times. Nevertheless, lubricants with low α coefficients are better at decreasing friction and the subsurface stresses.[6,36,37]

The α coefficient can be determined either directly by measuring viscosity as a function of pressure using a high-pressure viscometer or indirectly by experimentally determining film thickness with an optical interferometer. However, 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.[38−40] For these reasons among others, α values obtained using the direct and indirect approaches can show large discrepancies. Among the several definitions to obtain the pressure−viscosity coefficient from experimental viscosity values, we have chosen that given by Dowson and Higginson:[41]

$$\alpha(p) = \frac{1}{\eta}\left(\frac{\partial \eta}{\partial p}\right)_T \qquad (7)$$

This definition takes into account the local variation of the slope of the log η versus pressure curves. The α coefficient obtained from eq 7 has been plotted against pressure at different temperatures for both PAGs in Figure 4. The local pressure−viscosity coefficients for both polyethers decrease when the pressure or the temperature increases. Taking into account the temperature decreasing trend of the α values (see also Table 4) and the α data reported by Lawford[2] at 295 K and measured by Aderin et al.,[42] we could conclude that the pressure−viscosity coefficients of both PAGs are slightly higher that several monoend-capped and uncapped PO PAGs and quite higher than those of EO PAGs. Besides, the α values for the PAG lubricants studied here are lower that those of dipentaerythritol esters[17] and pentaerythritol esters[12,13,15] with linear side chains, com-

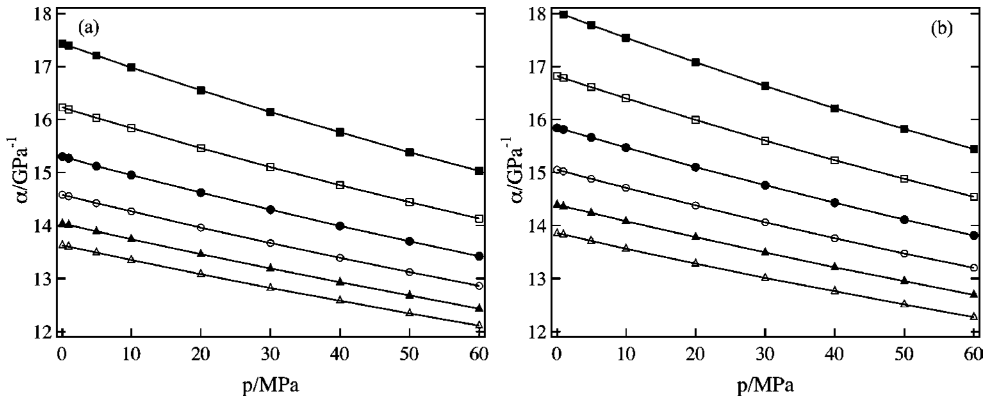

Figure 4. Local pressure−viscosity coefficient as a function of temperature and pressure for (a) PAG1 and (b) PAG2: ■, 313.15 K; □, 323.15 K; ●, 333.15 K; ○, 343.15 K; ▲, 353.15 K; and △, 363.15 K.

Table 4. Pressure−Viscosity Coefficient, α, and Temperature-Viscosity Coefficient, *β*, at Selected Pressures and Temperatures

		PAG1	PAG2
p/MPa	*T*/K	α (GPa^{-1})	
10	313.15	16.98	17.54
50	313.15	15.38	15.82
10	333.15	14.95	15.47
50	333.15	13.70	14.11
10	353.15	13.74	14.08
50	353.15	12.68	12.95
		$10^3\,\beta$ (K^{-1})	
10	313.15	39.47	39.02
50	313.15	41.03	40.47
10	333.15	29.33	29.98
50	333.15	30.42	31.11
10	353.15	22.62	23.74
50	353.15	23.32	24.59

pounds also widely used as base oils for lubricants for refrigeration systems.

Another essential property to characterize a lubricant is the temperature−viscosity coefficient, which is defined by the following expression:

$$\beta = -\frac{1}{\eta}\left(\frac{\partial \eta}{\partial T}\right)_p \qquad (8)$$

In Figure 5 the β coefficients for the PAG lubricants are plotted. The temperature−viscosity coefficients decrease with increasing temperature, whereas their pressure dependence is quite smooth. The temperature−viscosity coefficients are quite similar for both PAGs. The β coefficient changes very slightly with the increase of the molecular weight for these double end-capped PAGs (Table 4).

Furthermore, the VI characterizes the temperature dependence of the kinematic viscosity of the lubricant. A higher VI implies a smoother temperature viscosity dependence. The VI values obtained for both polyethers are quite high: 218 for PAG1 and 220 for PAG2, in agreement with the fact that VI increases with the molecular weight of the PAG.[2] Double-end-capped PAGs have also higher VI than monoend-capped or uncapped PAGs.

Roland and co-workers,[43−46] among other researchers,[47−51] have shown that, when expressed as a function of the product TV^{γ}, the viscosity for various glass-forming liquids, lubricants, ionic liquids, and polymers overlaps, that is, η is the only function of TV^{γ}

$$\eta(T, V) = \eta(T, p) = f(TV^{\gamma}) \qquad (9)$$

With this scaling we can not only interpolate and extrapolate experimental data but also know the value of the exponent γ for a given liquid.[44,52] This value reflects the magnitude of the intermolecular and intramolecular 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.[44]

For each PAG, the viscosity data collapsed onto a single master curve when plotted as a function of TV^{γ} (Figure 6). We determine the γ values by fitting the experimental data to the following equation:[49]

$$\eta(T, V) = \eta_0 \exp\left[\left(\frac{A}{TV^{\gamma}}\right)^{\phi}\right] \qquad (10)$$

where η_0, A, ϕ, and γ are constants. This equation satisfies the scaling property (eq 9) and also gives a good description of experimental data over a broad dynamic range, extending to T for which the behavior becomes Arrhenius. Casalini and Roland[53] observed that applying an analogous relation of eq 10 to relaxation times, the parameters ϕ and γ appear to be inversely correlated, that is, materials having a larger γ have a smaller value of the parameter ϕ. The same behavior is observed when eq 10 is applied to viscosity values as a function of the pressure.[54] From the fits of the experimental viscosity data to eq 10, one obtains γ of 4.15 for PAG1 and 4.25 for PAG2. In a previous work, we obtained for three double methyl-end-capped oligomers $CH_3O(CH_2CH_2O)_nCH_3$ with 2 to 4 EO units, that increasing the number of n provokes an important decrease in the values of the scaling parameter, as a result likely of the increasing of the dipole moment and of the number of bonds.[49] For PAG1 and PAG2, the values of γ are very close; this may indicate that the effect of increasing the number of ether groups has not an important effect when we change the number of PO units from 23 to 29.

This study complements those performed in previous works for pure pentaerythritol esters,[48] for two dipentaerythritol esters,[17] and for a number of molecular and ionic liquids elsewhere.[49] For all of these compounds the γ values are lower than 5.5 being the lowest γ values for dipentaerythritol pentanoate, DiPEC5, and dipentaerythritol heptanoate, DiPEC7 (Figure 6). This is in agreement with the size of their molecules and the intensity of their molecular forces, whereas for smaller

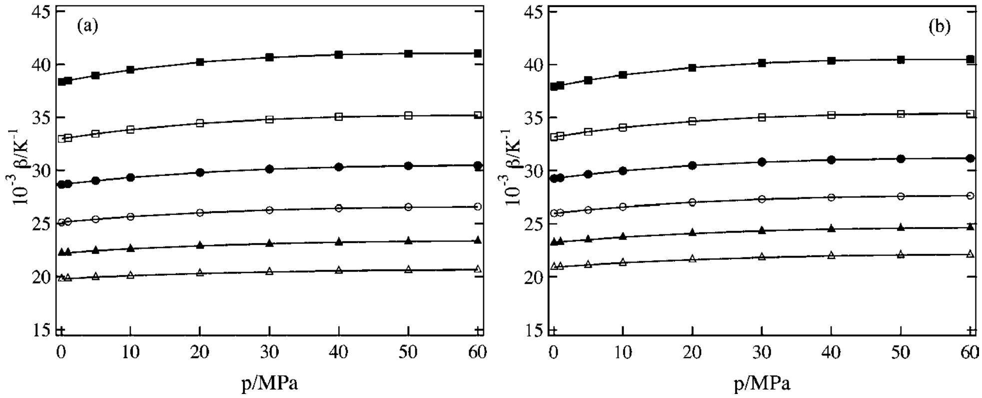

Figure 5. Temperature−viscosity coefficient as a function of temperature and pressure for (a) PAG1 and (b) PAG2: ■, 313.15 K; □, 323.15 K; ●, 333.15 K; ○, 343.15 K; ▲, 353.15 K; and △, 363.15 K.

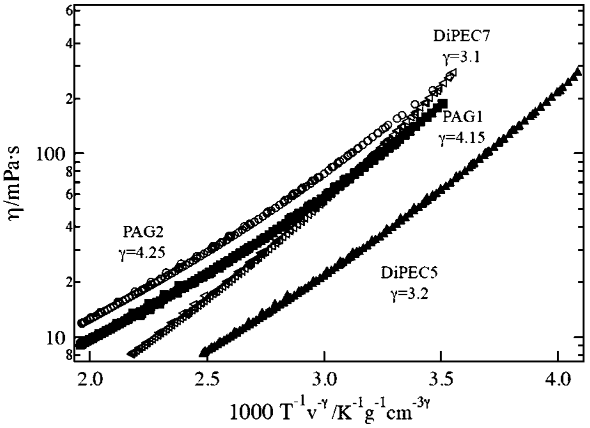

Figure 6. Superpositioned viscosities for ■, PAG1; ○, PAG2, ▲, DiPEC5, ▽, DiPEC7. The pressure ranges from ambient to 60 MPa.

molecules such as hexane with weaker molecular forces the γ value is 13.[49]

Conclusions

New viscosity data are reported for two PAG base lubricants. The viscosity measurements have been performed at high pressures with a rolling-ball technique and with a rotational viscometer at atmospheric pressure. The viscosity, the α and β coefficients, and the VI have been analyzed for the tested fluids. Empirical correlations are provided for the viscosities in terms of temperature and pressure. Moreover it has been verified that the viscosity is a unique function of TV^{γ} where the exponent γ is related to the steepness of the intermolecular repulsive potential, yielding scaling parameters of 4.15 and 4.25 for PAG1 and PAG2, respectively.

Acknowledgment

We are very grateful to Dr. S. J. Randles (Croda) for providing us the samples of both PAGs.

Literature Cited

(1) Pirro, D. M.; Wessol, A. A. *Lubrication Fundamentals*, 2nd ed.; Marcel Dekker, Inc.: 2001; p 540.

(2) Lawford, S. Polyalkylene Glycols. In *Synthetic, Mineral Oils, and Bio-Based Lubricants: Chemistry and Technology*; Rudnick, L. R., Ed.; Taylor and Francis: Boca Raton, FL, 2006; Vol. 111, pp 119−137.

(3) Randles, S. J. Refrigeration Lubricants. In *Synthetic, Mineral Oils, and Bio-Based Lubricants: Chemistry and Technology*; Rudnick, L. R., Ed.; Taylor and Francis: Boca Raton, FL, 2006; Vol. 111, pp 493−516.

(4) Kim, M. H.; Pettersen, J.; Bullard, C. W. Fundamental Process and System Desing Issues in CO_2 Vapor Compression Systems. *Prog. Energy Combust. Sci.* **2004**, *31*, 119–174.

(5) Mang, T.; Dresel, W. *Lubricants and Lubrication*; Wiley-VCH: New York, 2001.

(6) Larsson, R.; Kassfeldt, E.; Byheden, Å.; Norrby, T. Base fluid parameters for elastohydrodynamic lubrication and friction calculations and their influence on lubrication capability. *J. Synth. Lubr.* **2001**, *18*, 183–198.

(7) Errichello, R. Selecting Oils with High Pressure-Viscosity Coefficients Increase Bearing Life by more than Four Times. *Mach. Lubr.* **2004**, 200403.

(8) Aderin, M.; Johnston, G. J.; Spikes, H. A. The Elastohydrodynamic Properties of Some Advanced Non Hydrocarbon-Based Lubricants. *Lubr. Eng.* **1992**, *48*, 633–638.

(9) Chang, H. S.; Spikes, H. A.; Bunemann, T. F. The shear stress properties of ester lubricants in elastohydrodynamic contacts. *J. Synth. Lubr.* **2006**, *9*, 91–114.

(10) Fandiño, O.; Lugo, L.; Comunas, M. J. P.; Lopez, E. R.; Fernandez, J. Temperature and pressure dependences of volumetric properties of two poly(propylene glycol) dimethyl ether lubricants. *J. Chem. Thermodyn.* **2010**, *42*, 84–89.

(11) Räder, H. J.; Schrepp, W. MALDI-TOF mass spectrometry in the analysis of synthetic polymers. *Acta Polym.* **1998**, *49*, 272–293.

(12) Lugo, L.; Canet, X.; Comuñas, M. J. P.; Pensado, A. S.; Fernández, J. Dynamic Viscosity under Pressure for Mixtures of Pentaerythritol Ester Lubricants with 32 Viscosity Grade. Measurements and Modelling. *Ind. Eng. Chem. Res.* **2007**, *46*, 1826–1835.

(13) Pensado, A. S.; Comuñas, 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.

(14) Pensado, A. S.; Comuñas, M. J. P.; Lugo, L.; Fernández, J. Experimental Dynamic Viscosities of 2,3-Dimethylpentane up to 60 MPa and from (303.15 to 353.15) K Using a Rolling-Ball Viscometer. *J. Chem. Eng. Data* **2005**, *50*, 849–855.

(15) Pensado, A. S.; Comuñas, M. J. P.; Lugo, L.; Fernández, J. High Pressure Characterization of Dynamic Viscosity and Derived Properties for Squalane and Two Pentaerythritol Ester Lubricants: Pentaerythritol Tetra-2-ethylhexanoate and Pentaerythritol Tetranonanoate. *Ind. Eng. Chem. Res.* **2006**, *45*, 2394–2404.

(16) Paredes, X.; Fandino, O.; Comunas, M. J. P.; Pensado, A. S.; Fernandez, J. Study of the effects of pressure on the viscosity and density of diisodecyl phthalate. *J. Chem. Thermodyn.* **2009**, *41*, 1007–1015.

(17) Paredes, X.; Pensado, A. S.; Comuñas, M. J. P.; Fernández, J. Experimental Dynamic Viscosities of Dipentaerythritol Ester Lubricants at High Pressure. *J. Chem. Eng. Data* **2010**; DOI: 10.1021/je100057b.

(18) Fandiño, O.; Lugo, L.; Comuñas, M. J. P.; López, E. R.; Fernández, J. Temperature and pressure dependences of volumetric properties of two poly(propylene glycol) dimethyl ether lubricants. *J. Chem. Thermodyn.* **2010**, *42*, 84–89.

(19) Comuñas, M. J. P.; Baylaucq, A.; Boned, C.; Fernández, J. High-Pressure Measurements of the Viscosity and Density of Two Polyethers and Two Dialkyl Carbonates at High Pressures. *Int. J. Thermophys.* **2001**, *22*, 749–768.

(20) Marquardt, D. W. An Algorithm for Least-Squares Estimation of Nonlinear Parameters. *J. Soc. Ind. Appl. Math.* **1963**, *11*, 431–441.

(21) Paluch, M.; Hensel-Bielowka, S.; Ziolo, J. Effect of pressure on fragility and glass transition temperature in fragile glass-former. *J. Chem. Phys.* **1999**, *110*, 10978–10981.

(22) Capaccioli, S.; Lucchesi, M.; Casalini, R.; Presto, S.; Rolla, P. A.; Viciosa, M. T.; Corezzi, S.; Fioretto, D. Pressure and temperature dependences of the dynamics of glass formers studied by broad-band dielectric spectroscopy. *Philos. Magn. B* **2002**, *82*, 651–662.

(23) Patkowski, A.; Paluch, M.; Gapinski, J. Relationship between T_0, T_g and their pressure dependence for supercooled liquids. *J. Non-Cryst. Solids* **2003**, *330*, 259–263.

(24) Kriegs, H.; Gapinski, J.; Meier, G.; Paluch, M.; Pawlus, S.; Patkowski, A. Pressure effects on the α and α′ relaxations in polymethylphenylsiloxane. *J. Chem. Phys.* **2006**, 124.

(25) Dlubek, G.; Kilburn, D.; Alam, M. A. Temperature and Pressure Dependence of α-Relaxation and Free Volume in Poly(vinyl acetate). *Macromol. Chem. Phys.* **2005**, *206*, 818–826.

(26) Patkowski, A.; Gapiński, J.; Meier, G. Dynamics of supercooled van der Waals liquid under pressure. A dynamic light scattering study. *Colloid Polym. Sci.* **2004**, *282*, 874–881.

(27) Paluch, M.; Patkowski, A.; Fischer, E. W. Temperature and Pressure Scaling of the α Relaxation Process in Fragile Glass Formers: A Dynamic Light Scattering Study. *Phys. Rev. Lett.* **2000**, *85*, 2140.

(28) Casalini, R.; Capaccioli, S.; Lucchesi, M.; Rolla, P. A.; Corezzi, S. Pressure dependence of structural relaxation time in terms of the Adam-Gibbs model. *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.* **2001**, *63*, 031207.

(29) Drozd-Rzoska, A.; Rzoska, S. J.; Roland, C. M.; Imre, A. R. On the pressure evolution of dynamic properties of supercooled liquids. *J. Phys.: Condens. Matter* **2008**, *20*, 244103.

(30) Harris, K. R.; Kanakubo, M.; Woolf, L. A. Temperature and Pressure Dependence of the Viscosity of the Ionic Liquids 1-Butyl-3-methylimidazolium Tetrafluoroborate: Viscosity and Density Relationships in Ionic Liquids. *J. Chem. Eng. Data* **2007**, *52*, 2425–2430.

(31) Harris, K. R.; Woolf, L. A.; Kanakubo, M. Temperature and Pressure Dependence of the Viscosity of the Ionic Liquid 1-Butyl-3-methylimidazolium Hexafluorophosphate. *J. Chem. Eng. Data* **2005**, *50*, 1777–1782.

(32) Harris, K. R.; Kanakubo, M.; Woolf, L. A. Temperature and Pressure Dependence of the Viscosity of the Ionic Liquids 1-Methyl-3-octylimidazolium Hexafluorophosphate and 1-Methyl-3-octylimidazolium Tetrafluoroborate. *J. Chem. Eng. Data* **2006**, *51*, 1161–1167.

(33) Harris, K. R.; Kanakubo, M.; Woolf, L. A. Temperature and Pressure Dependence of the Viscosity of the Ionic Liquids 1-Hexyl-3-methylimidazolium Hexafluorophosphate and 1-Butyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide. *J. Chem. Eng. Data* **2007**, *52*, 1080–1085.

(34) Mattsson, J.; Bergman, R.; Jacobsson, P.; Börjesson, L. Influence of Chain Length on the α−β Bifurcation in Oligomeric Glass Formers. *Phys. Rev. Lett.* **2005**, *94*, 165701.

(35) Spikes, H. A. A Thermodynamic Approach to Viscosity. *Tribol. Trans.* **1990**, *33*, 140–148.

(36) Höglund, E. Influence of lubricant properties on elastohydrodynamic lubrication. *Wear* **1999**, *232*, 176–184.

(37) Cardoso, N. F. R.; Martins, R. C.; Seabra, J. H. O.; Igartua, A.; Rodríguez, J. C.; Luther, R. Micropitting performance of nitrided steel gears lubricated with mineral and ester oils. *Tribol. Int.* **2009**, *42*, 77–87.

(38) Bair, S.; Liu, Y. C.; Wang, Q. J. The pressure-viscosity coefficient for Newtonian EHL film thickness with general piezoviscous response. *J. Tribol.* **2006**, *128*, 624–631.

(39) Liu, Y.; Wang, Q. J.; Wang, W.; Hu, Y.; Zhu, D.; Krupka, I.; Hartl, M. EHL simulation using the free-volume viscosity model. *Tribol. Lett.* **2006**, *23*, 27–37.

(40) Bair, S.; Fernandez, J.; Khonsari, M. M.; Krupka, I.; Qureshi, F.; Vergne, P.; Wang, Q. J. An argument for a change in elastohydrodynamic lubrication philosophy. *Proc. Inst. Mech. Eng., Part J* **2009**, *223*, I–II.

(41) Dowson, D.; Higginson, G. R. *Elastohydrodynamic Lubrication*; Pergamon Press: Oxford, 1966.

(42) Aderin, M. E.; Johnston, G. J.; Spikes, H. A.; Balson, T. G.; Emery, M. G. In 8th International Colloquium on Tribology, Tribology 2000, Esslingen, Germany, 1992.

(43) Roland, C. M.; Bogoslovov, R. B.; Casalini, R.; Ellis, A. R.; Bair, S.; Rzoska, S. J.; Czuprynski, K.; Urban, S. Thermodynamic scaling and the characteristic relaxation time at the phase transition of liquid crystals. *J. Chem. Phys.* **2008**, *128*, 224506–9.

(44) Roland, C. M.; Bair, S.; Casalini, R. Thermodynamic scaling of the viscosity of van der Waals, H-bonded, and ionic liquids. *J. Chem. Phys.* **2006**, *125*, 124508/1–124508/11.

(45) Casalini, R.; Roland, C. M. Scaling of the supercooled dynamics and its relation to the pressure dependences of the dynamic crossover and the fragility of glass formers. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2005**, *71*, 014210/1−014210/10.

(46) Casalini, R.; Bair, S. The inflection point in the pressure dependence of viscosity under high pressure: A comprehensive study of the temperature and pressure dependence of the viscosity of propylene carbonate. *J. Chem. Phys.* **2008**, *128*, 084511−7.

(47) Tarjus, G.; Kivelson, D.; Mossa, S.; Alba-Simionesco, C. Disentangling density and temperature effects in the viscous slowing down of glassforming liquids. *J. Chem. Phys.* **2004**, *120*, 6135–6141.

(48) Fandiño, O.; Comuñas, M. J. P.; Lugo, L.; López, E. R.; Fernández, J. Density Measurements under Pressure for Mixtures of Pentaerythritol Ester Lubricants. Analysis of a Density-Viscosity Relationship. *J. Chem. Eng. Data* **2007**, *52*, 1429–1436.

(49) Pensado, A. S.; Padua, A. A. H.; Comuñas, M. J. P.; Fernandez, J. Relationship between viscosity coefficients and volumetric properties using a scaling concept for molecular and ionic liquids. *J. Phys. Chem. B* **2008**, *112*, 5563–5574.

(50) Harris, K. R. Temperature and Pressure Dependence of the Viscosities of 2-Ethylhexyl Benzoate, Bis(2-ethylhexyl) Phthalate, 2,6,10,15,19,23-Hexamethyltetracosane (Squalane), and Diisodecyl Phthalate. *J. Chem. Eng. Data* **2009**, *54*, 2729–2738.

(51) Harris, K. R. The fractional Stokes−Einstein equation: Application to Lennard-Jones, molecular, and ionic liquids. *J. Chem. Phys.* **2009**, *131*, 054503−8.

(52) Roland, C. M.; Hensel-Bielowka, S.; Paluch, M.; Casalini, R. Supercooled dynamics of glass-forming liquids and polymers under hydrostatic pressure. *Rep. Prog. Phys.* **2005**, *68*, 1405–1478.

(53) Casalini, R.; Roland, C. M. An equation for the description of volume and temperature dependences of the dynamics of supercooled liquids and polymer melts. *J. Non-Cryst. Solids* **2007**, *353*, 3936–3939.

(54) Pensado, A. S.; Comuñas, M. J. P.; López, E. R.; Pádua, A. A. H.; Fernández, J. Scaling Termodinámico de las propiedades de transporte de líquidos. In *La investigación del Grupo Especializado de Termodinámica de las Reales Sociedades Españolas de Física y de Química*; Urieta, J. S., Pardo, J. I., Mainar, A. M., Eds.; Real Sociedad Española de Física: Madrid, Spain, 2008; pp 49−63.

Received for review March 24, 2010. Accepted July 17, 2010. This work was supported by the Spanish Science and Technology Ministry (CTQ2005-09176-C02-01/PPQ) and Xunta de Galicia (PGIDIT05-TAM20601PR and PGIDIT06PXIC20640PN). Equipment funding from the SXID Xunta de Galicia is also acknowledged. The participation of A.S.P. was made possible by an Ánxeles Alvariño fellowship from DXID, Xunta de Galicia.

JE100285A