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PrT measurements and EoS predictions of ester lubricants up to 45 MPa

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Abstract

The density of pentaerythritol tetrapentanoate has been measured under pressure using a vibrating tube densimeter. The measurements have been performed at nine temperatures in the range 278.15 to 353.15 K and eleven isobars up to 45 MPa. The uncertainty in the measured densities is estimated to be $\pm 1 \cdot 10^{-4} \text{ g} \cdot \text{cm}^{-3}$. The measured data have been used to study the behavior and influence of temperature and pressure on the isothermal compressibility, the thermal expansion coefficient and the internal pressure. A correction factor, due to the viscosity of the sample, was applied to the density experimental values. The prediction ability of Sako-Wu-Prausnitz (SWP) equation of state (EoS) combined with the group contribution method of Elvassore et al. was analysed for diesters as dialkyl sebacates or 1,10-decanediol diesters, triesters as triglycerides or trimethylolethane triesters, and pentaerythritol tetraesters. For this purpose, densities at pressures up to 45 MPa and several temperatures were used for four tetraesters, whereas for the other compounds density data at atmospheric pressure and several temperatures have been considered due to the unavailability of high pressure data. The ability prediction of Soave-Redlich-Kwong (SRK) and Peng-Robinson (PR) for densities at broad ranges of temperatures and pressures was also analysed for some pentaerythritol tetraesters, for which critical constants and acentric factor were estimated in the literature.

Keywords: Density; High pressure; Temperature; esters; Lubricant; Equation of state

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1. Introduction

Due to their lubricity, thermal stability and biodegradability, polyol esters, POEs, are used in a wide variety of applications, such as refrigeration compressors, aviation, greases, air compressors, metalworking, fire resistant and biodegradable hydraulic fluids. Many POE lubricants based mainly on pentaerythritol esters are used as refrigeration oils with HFCs and CO₂ refrigerants. Thermophysical properties of the POE, density among them, are needed to develop efficient lubricants for each application and to provide models of volumetric, phase and viscosity behaviour to the designers of refrigeration systems and compressors. In the literature, there are some suggestions on how the structure of the compressor oil will affect the behaviour of the refrigerant-lubricant mixtures. For example, Randles [1] has analysed the influence of the size and branching of the chains of ester lubricants on the viscosity index, pour and flash points as well as elastomer compatibility. On the other hand, one of the problems that is found to develop and to apply models of volumetric, phase and viscosity behaviour involving lubricants is the characterization of their components, that is, how to determine the parameters of the equation de state (EoS) for the lubricants.

In order to contribute to this important task, in this work, density measurements of pentaerythritol tetrapentanoate, PEC5, from 278.15 to 353.15 K and from 0.1 to 45 MPa will be presented. Densities, ρ , were measured with an Anton Paar densimeter. A new correction factor due to the viscosity was applied to the density experimental values. From the density correlation, the thermal expansion coefficient, α_p , isothermal compressibility, k_T , and internal pressure, π , were determined. Furthermore, following the previous papers of Shobha and Kishore [2] and Phillips and Mattamal [3] the influence of the molecular structure on the density at different temperatures and pressures has been studied using the data available in the literature [2-5] for several type

of esters together with the experimental values of PEC5, pentaerythritol tetraheptanoate, PEC7, pentaerythritol tetranonanoate, PEC9 and pentaerythritol tetra(2-ethylhexanoate), PEB8, reported in this work and in the previous ones [6,7]. In addition, all these density data were used to verify the Sako-Wu-Prausnitz EoS, SWP, linked to the Elvassore et al. [8] method for the determination of the EoS characteristic parameters. Furthermore, Soave-Redlich-Kwong (SRK) [9] and Peng-Robinson (PR) [10] equations were applied taking the critical parameters estimated by Teodorescu et al. [11] and by García et al. [12] in order to evaluate the reliability of these EoS to predict the pressure dependence of the density of PEC5, PEC9 and PEB8.

2. Experimental Section

PEC5 was synthesized by a reaction between pentanoic acid and pentaerythritol catalysed by p-toluenesulfonic acid. This method was used previously by Black and Gunstone [13] and by Wahlström and Vamling [5]. The distilled product was analysed by ^1H NMR, ^{13}C NMR, and IR spectroscopies, and the purity was estimated to be bigger than 95%.

The density was measured with an Anton-Paar DMA 512P high-pressure density measuring cell. A schematic and detailed description of the experimental setup and procedures can be found in [14,15]. In the case of viscous liquids it is needed to apply a correction factor to the density value obtained from the calibration performed using one or two non-viscous liquids [6,16,17]. We have used the same procedure that in our previous work [6], which was recommended by Anton Paar for DMA 512P densimeter.

The viscosity values for PEC5 have been taken from Pensado *et al.* [18]. The correction factor, $\Delta\rho$, ranges $6\cdot 10^{-5}$ to $5\cdot 10^{-4}$ $\text{g}\cdot\text{cm}^{-3}$. Taking into account the different sources of error, the estimated density uncertainty is $\pm 1\cdot 10^{-4}$ $\text{g}\cdot\text{cm}^{-3}$.

3. Analysis of the Experimental Results

The experimental $P\rho T$ values for PEC5 along nine isotherms: at 278.15 K and between (283.15 and 353.15) K at 10 K intervals and along eleven isobars at pressures up to 45 MPa were fitted with a modified Tammann-Tait equation [19]. The standard deviations obtained for the r values at atmospheric pressures, S , and at higher pressures, S^* , with the Tammann-Tait correlations are $7 \cdot 10^{-5}$ and $6 \cdot 10^{-5} \text{ g}\cdot\text{cm}^{-3}$ respectively. Fig. 1 shows the experimental density values together with the correlation curves. The relative deviations between the experimental data for this compound and those calculated with the Tammann-Tait equation are presented in Fig. 2.

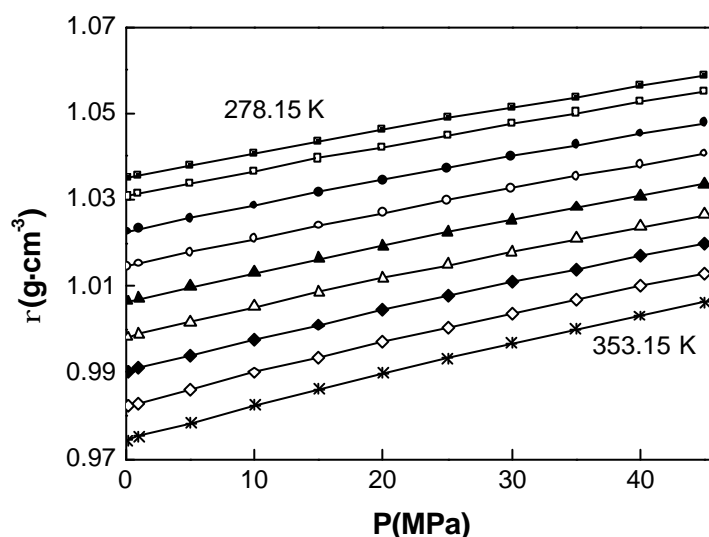


Fig. 1. Experimental density data for PEC5 at several temperatures: (■) 278.15 K, (□) 283.15 K, (●) 293.15 K, (○) 303.15 K, (▲) 313.15 K, (△) 323.15 K, (◆) 333.15 K, (◇) 343.15 K, (*) 353.15 K. Straight lines: Tammann-Tait correlation

Several authors [2,4] have previously measured the densities of PEC5 at several temperatures and at atmospheric pressure. Fig. 3 shows the agreement between our experimental data and those of literature. Until our knowledge, no density values at different pressure than the atmospheric one exist for this compound.

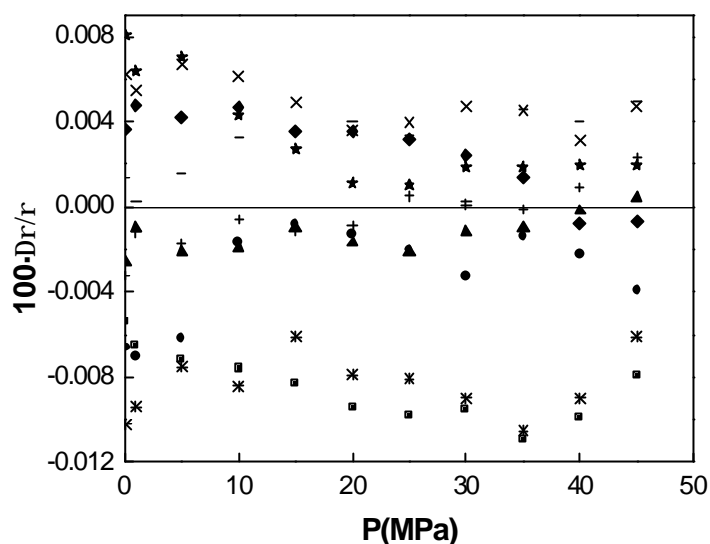


Fig. 2. Relative deviations between the experimental and Tammann Tait correlated compressed density data for PEC5: (◆) 278.15 K, (●) 283.15 K, (▲) 293.15 K, (★) 303.15 K, (×) 313.15 K, (*) 323.15 K, (−) 333.15 K, (+) 343.15 K, (■) 353.15 K.

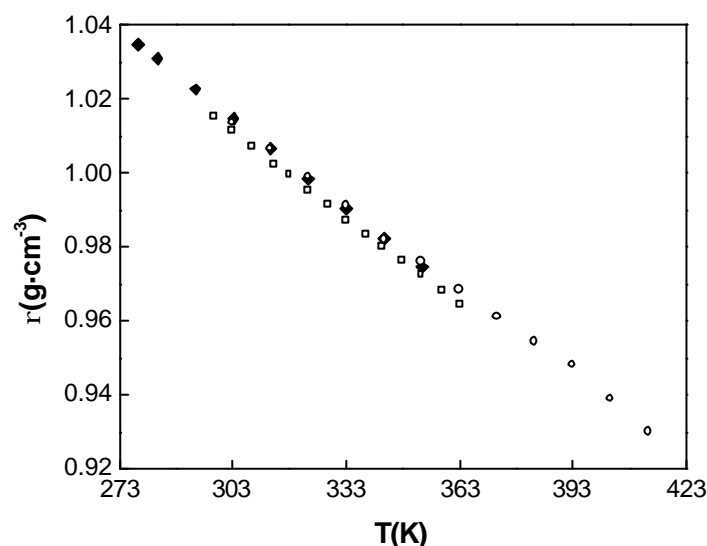


Fig. 3. Experimental density values and literature data at atmospheric pressure: (○) Shobha and Kishore [2], (□) Whalström and Vamling [4], (◆) This work.

For pentaerythritol esters of linear chains, in all the temperature and pressure range it was found the following order for r values, $\text{PEC5} > \text{PEC7} > \text{PEC9}$ (Fig. 4). This is due to when the number of methylene groups increases, intermolecular forces among the ester groups became less intense, which also diminishes the efficiency of the molecular packing, increasing the free volume [2,7]. Moreover, although molecular

weight increases at the same time than length of the acid chains, the ratio of heavy atoms to the number of carbons in the molecule diminishes, which also contributes to lower density values [7].

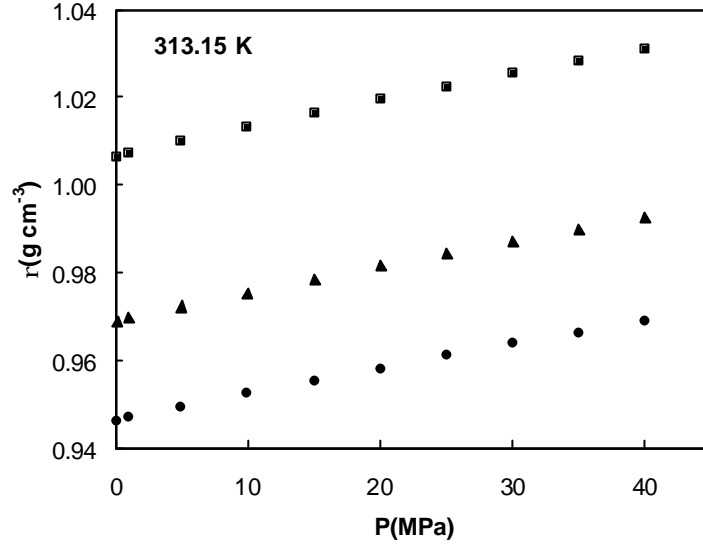


Fig. 4. Experimental density data against the pressure at 313.15 K for several pentaerythritol esters: (■) PEC5, (▲) PEC7, (●) PEC9.

The isothermal compressibility, $k_T = (1/r)(\partial r / \partial P)_T$, the thermal expansion coefficient, $\alpha_P = -(1/r)(\partial r / \partial T)_P$, and the internal pressure, $p = T(\alpha_P / k_T) - P$, were determined by using the Tammann-Tait equation with the parameters determined in this work.

In Fig. 5 it can be seen that for PEC5, k_T increases when the temperature increases and decreases when the pressure increases. This behavior is similar to that found for PEC7, PEC9 and PEB8. The four POEs are slightly expansible and compressible. In all the T,P conditions, α_P , k_T and π values of the linear pentaerythritol esters compounds (PEC5 to PEC9) diminishes with increasing of the CH₂ groups. The increase of branching degree leads to lower α_P and π values and higher isothermal compressibilities [7].

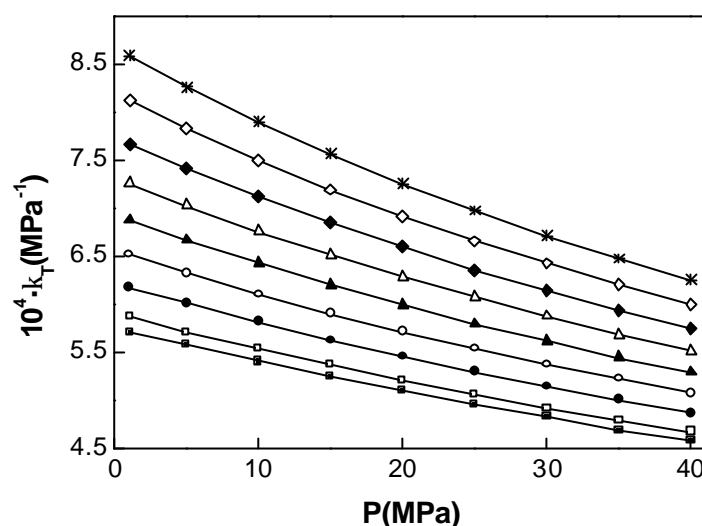


Fig. 5. Isothermal compressibility against the pressure for PEC5 at: (■) 278.15 K, (□) 283.15 K, (●) 293.15 K, (○) 303.15 K, (▲) 313.15 K, (△) 323.15 K, (◆) 333.15 K, (◇) 343.15 K, (*) 353.15 K.

4. Analysis of the equation of state predictions

These density data at high pressures together with a data base of densities at atmospheric pressure of 40 esters of six types: dialkyl sebacates $\text{CH}_3(\text{CH}_2)_x\text{COO}(\text{CH}_2)_8\text{COO}(\text{CH}_2)_x\text{CH}_3$, 1,10-decanediol diesters $\text{CH}_3(\text{CH}_2)_x\text{COO}(\text{CH}_2)_{10}\text{COO}(\text{CH}_2)_x\text{CH}_3$, triglycerides $\text{CH}_3(\text{CH}_2)_x\text{COOCH}[\text{CH}_2\text{COO}(\text{CH}_2)_x\text{CH}_3]_2$, trimethylolethane triesters $\text{CH}_3\text{C}[\text{CH}_2\text{COO}(\text{CH}_2)_x\text{CH}_3]_3$, pentaerythritol tetraesters $\text{C}[\text{CH}_2\text{COO}(\text{CH}_2)_x\text{CH}_3]_4$ and linear oligomer of esters of poly(hexamethylene sebacate) $(\text{CH}_3(\text{CH}_2)_5\text{OOC}(\text{CH}_2)_8\text{COO}[(\text{CH}_2)_6\text{OOC}(\text{CH}_2)_8\text{COO}]_x\text{-(CH}_2)_5\text{CH}_3)$ were used to study the ability prediction of the Sako-Wu-Prausnitz EoS, SWP, combined to the Elvassore et al. method [8] for the determination of the EoS characteristic parameters. For all the families except for pentaerythritol tetraesters and triglycerides the average absolute deviation $\text{AAD} = |\text{Bias}|$. The densities of dialkyl sebacates, 1,10-decanediol diesters and oligomer ester of poly(hexamethylene sebacate) are always underpredicted ($\text{AAD} = \text{Bias}$) by SWP, whereas those of trimethylolethane triesters are always overpredicted ($\text{AAD} = -\text{Bias}$). For five triglycerides the predicted

densities are higher than the experimental ones. For the pentaerythritol tetraesters of the shorter linear chains (pentaerythritol tetraethanoate, PEC2, pentaerythritol tetrapropanoate, PEC3 and pentaerythritol tetrabutanoate, PEC4) as well as for the branched POEs, PEB6 (pentaerythritol (2-ethyl butanoate)) and PEB8, SWP also overpredicts the density values ($AAD = -Bias$) whereas the opposite happens with PEC10 (pentaerythritol tetradecanoate). For the others POEs, the predictions are not biased ($|Bias| < AAD$). Fig. 6 shows experimental densities of dialkyl sebacate esters (DSs) at atmospheric pressure together with the predictions of SWP. This EoS reproduces quite well the trend with the temperature. For the other esters, SWP equation gives similar reproduction of the temperature trends at atmospheric pressure.

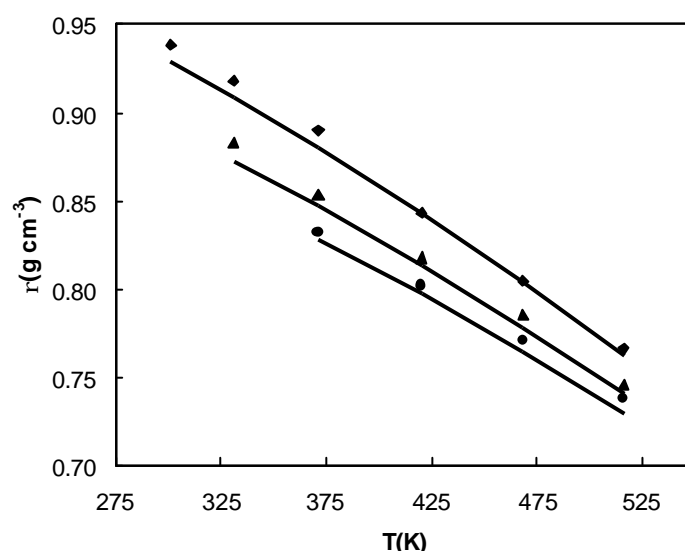


Fig. 6. Experimental and predicted densities for dialkyl sebacate esters (DSs) at atmospheric pressure; experimental points [3]: (◆) di-n-butyl sebacate, (▲) di-n-decyl sebacate, (●) di-n-octadecyl sebacate; predicted densities with SWP EoS: (—).

In the case of the pentaerythritol esters PEC5, PEC7, PEB8 and PEC9 experimental density data in a wide range of pressures and temperatures (from 1 MPa up to 45 MPa and between 278.15 K and 353.15 K) were also used to analyze the goodness of the SWP, SRK and PR predictions, presenting the results similar AADs for the three EoS. In the case of SWP the worst predictions were for PEB8, for which all

the predicted density data are lower than the experimental points and the maximum deviation is 2.3 % (at 45 MPa and 353.15 K). In Fig. 7 relative deviations between the experimental data and those calculated with the SWP equation for PEC7 are plotted. It can be seen that at the lower temperatures (278.15 and 283.15 K) the deviations decrease when the pressure increases. By the contrary, at the higher temperatures (333.15-353.15) K the deviations increases when the pressure grows. At the intermediate temperatures the deviation varies non-monotonically with pressure. In addition, for the SWP EoS, in the case of PEC5 the deviations increase with the pressure except for the two lower temperatures, where the deviations decrease at lower pressures, whereas for PEC9 firstly the deviations decrease with the pressure up to 343.15 K and then increase; finally, for PEB8 the deviations always increase with the pressure.

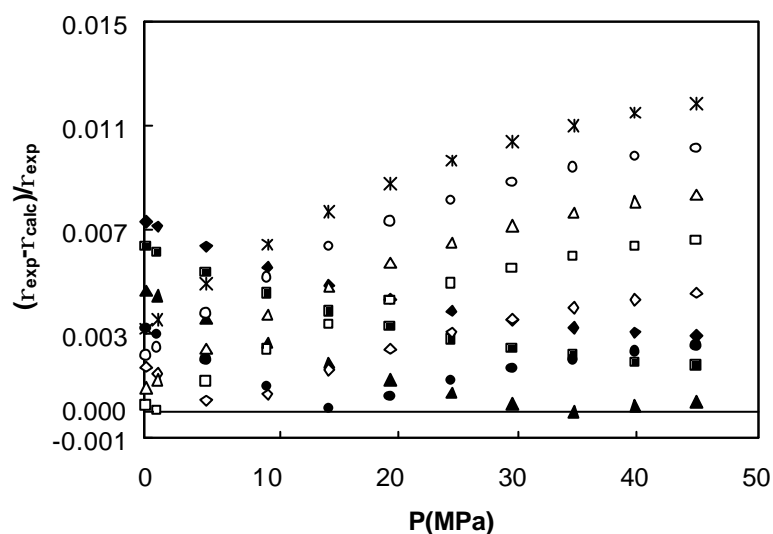


Fig. 7. Relative deviations between the experimental data and those calculated with SWP EoS for PEC7 against pressure: (◆) 278.15 K, (■) 283.15 K, (▲) 293.15 K, (●) 303.15 K, (◇) 313.15 K, (□) 323.15 K, (△) 333.15 K, (○) 343.15 K, (*) 353.15 K.

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