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Experimental density and PC-SAFT modeling of Krytox® (perfluoropolyether) at pressures to 275 MPa and temperatures to 533 K

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ABSTRACT

Density data from 298 to 533 K and to 275 MPa are reported for Krytox® GPL 102, a poly(perfluoropropyl ether) (PFPE) with a CF_3-branched fluoropropylether repeat group. The Tait equation fit to each density isotherm have mean absolute percent deviations (MAPD) between 0.11 and 0.30% with standard deviations (SD) not exceeding 0.20%. The perturbed-chain statistical associating fluid theory (PC-SAFT) fit to the density data has an MAPD of 0.67% and an SD of 0.67%. Likewise the PC-SAFT fit to previously reported density data of Demnum®, a PFPE with an n-fluoropropylether repeat group, has an MAPD of 0.22% and a SD of 0.21% for Demnum® S-20 and an MAPD of 0.27% with a SD of 0.14% for Demnum® S-65. The trends exhibited by the PC-SAFT pure component parameters obtained from the fits of these three PFPEs are similar to those reported for linear and branched hydrocarbons with the same number of carbons.

1. Introduction

Perfluoropolyethers (PFPEs) are a class of synthetic oils used in a variety of high-temperature lubricant and hydraulic fluid applications [1–5]. The physical properties of PFPEs that make them excellent lubricants at extreme conditions include their low vapor pressure, low surface energy, good thermal stability, and non-flammability [3–5]. PFPEs only contain carbon, oxygen, and fluorine atoms and are inert to most chemicals including oxidizing agents, which makes PFPEs compatible in various chemical environments under extreme conditions [6,7].

Krytox® GPL 102, a branched perfluoropolyether, manufactured by DuPont, is a fluorine end-capped, homopolymer of hexafluoropropylene epoxide, with a reported molecular weight of 1726 g/mol. The viscosity characteristics of Krytox® GPL 102 closely mimic those of light oils produced in ultra-deep well formations and, therefore, this PFPE can be used as a representative standard for these light oils [8,9] There is a need for high-temperature, high-pressure density data for this Krytox® oil, since the density is used to estimate the oil viscosity [10–12]. The present study reports experimental high-temperature, high-pressure Krytox® GPL 102 density to temperatures of 533 K and pressures of 275 MPa. The density data are obtained using a variable-volume, high-pressure cell previously used to obtain density data for n-alkanes from pentane to eicosane [13,14].

The modified Tait equation [15] is fit to the Krytox® density data obtained in this study to determine values for the two constants used with this equation. One of the parameters, B, has dimensions of pressure and varies with temperature and the other parameter, C, is a dimensionless constant whose value typically remains fixed for compounds from the same chemical family. The modified Tait equation is a reliable method to calculate liquid densities over wide ranges of temperature and pressure.

The Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT), proposed by Gross and Sadowski [16], is also fit to Krytox® density data to obtain values for the three pure component parameters used with this equation. The PC-SAFT equation of state (EOS) represents the Helmholtz free energy as a sum of terms accounting for hard sphere repulsion, chain connectivity, dispersion interactions, and segment–segment association. In the present study the segment–segment association term is ignored since Krytox® does not self-associate. Hence, the thermodynamic properties of non-associating fluids are predicted with the PC-SAFT EOS using parameters accounting for the number of segments in the molecule, m, the temperature-independent segment diameter, σ, and

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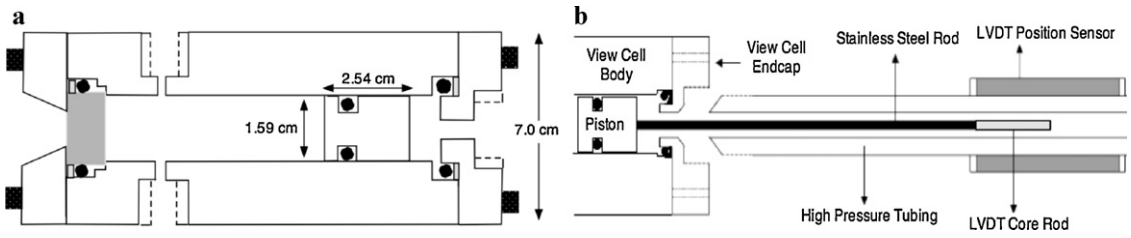


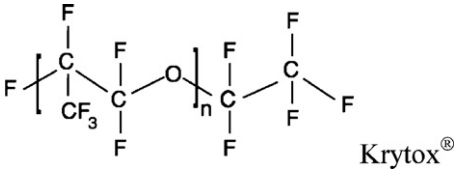
Fig. 1. Schematic diagram of (A) the high-pressure view cell used in this study and (B) the linear variable differential transformer (LVDT) used for volume measurements.

interaction energy, ε/k_B. For polymer systems, these parameters are typically obtained by fitting the equation to experimental density data or to a combination of polymer density data and phase equilibria data for polymer–solvent mixtures [17–20]. The PC-SAFT EOS has been successfully used to predict the thermodynamic properties of many different kinds of polymer systems [17–26]. In certain instances group contribution (GC) methods have been used with the PC-SAFT EOS to estimate values for the three pure component parameters [17,27] rather than fitting the EOS to experimental data. However, to the best of our knowledge, the GC approach has not been used with the PC-SAFT equation for fluorinated polymers, although the GC approach has been used with PC-SAFT to model the behavior of low-molecular weight, linear perfluoroalkanes [28,29]. Unfortunately, GC parameter values for —CF< and —CF_2O— groups are not available, which would have allowed for the determination of parameters for Krytox®. Hence, the three pure component parameters for Krytox® are obtained by fitting the PC-SAFT EOS directly to density data obtained in this study. The PC-SAFT EOS is also fit to literature density data for Demnum®, a linear PFPE [30], to obtain values for m, σ, and ε. The Demnum® pure component parameters are compared to those for Krytox®, a branched PFPE, to ascertain if these parameters vary in a manner consistent with that observed for other linear and branched compounds from the same chemical family.

2. Experimental

2.1. Material

DuPont Corporation donated the Krytox® GPL 102 PFPE oil which has the structure shown here and an averaged molecular weight of 1726 g/mol with an average "n" value of 10. The Krytox® oil was used as received.



Krytox®

2.2. Apparatus

Fig. 1 shows a schematic diagram of the high-pressure view cell used in this study, which has been described in detail elsewhere [13]. The cell, constructed from Nitronic 50, a high nickel content steel, has a 7.0 cm external diameter (OD), a 1.59 cm internal diameter, and a ~35 ml working volume. A 1.9 cm OD by 1.9 cm thick sapphire window is fitted to one end of the cell and sealed with an elastomeric O-ring. Prior to their use, the elastomeric O-rings used in this study are soaked in Krytox® oil for at least 6 h at 353 K and then at room temperature for a further 24 h. The cell contents are compressed to the desired operating pressure with an internal piston, displaced with pressurized water using a high-pressure generator. The system pressure is measured on the water-side of the piston using a pressure transducer (Viatran Corporation, Model 245, 0–345 MPa, accurate to ±0.35 MPa) calibrated against a Heise pressure gauge (Heise Corporation, Model CC, 0–68.9 MPa, accurate to ±0.07 MPa). The transducer reading is within ±0.07 MPa of the Heise gauge to pressures of ~56.5 MPa, hence, the transducer is considered accurate to ±0.07 MPa to pressures of 56 MPa and to ±0.35 MPa for pressures from 56 to 275 MPa. The reported system pressure is equal to the transducer reading plus 0.07 MPa, which is the pressure needed to move the piston as determined by measuring the pressure on each side of the piston during a calibration experiment. The type-k thermocouple used to measure the temperature of the fluid in the view cell is calibrated, at four different temperatures, against a precision immersion thermometer (Fisher Scientific, 308–473×, precise to 0.1 K, accurate to better than ±0.10 K, recalibrated by ThermoFisher Scientific Company at four different temperatures using methods traceable to NIST standards). The experimentally observed temperature variation for each reported isotherm is within ±0.16 K.

The internal volume of the cell is determined using a linear, variable, differential transformer (LVDT, Schaevitz Corp., Model 2000 HR) that tracks the location of the internal floating piston as shown in Fig. 1B. Connected to the piston is a rod with a magnetic end piece, called a core that is tracked by the LVDT located outside the high-temperature bath (not shown here). The view cell volume is calibrated at 323, 423, and 523 K using n-decane whose density has been reported by NIST to a maximum value of 770 kg m^{-3} or to maximum operating conditions of 800 MPa and 673 K [31]. Before performing a density measurement, the cell is flushed three times with CO_2 to remove any residual air that is not expected to dissolve in the Krytox® oil. The small amount of CO_2 remaining in the cell, approximately 0.06 g, is not expected to have a significant effect on the reported Krytox® densities since CO_2 will readily dissolve in the 14.0 to 20.0 ± 0.0001 g of Krytox® oil loaded into the cell for a typical experiment. The estimated accumulated error in the reported Krytox® density is within ±0.70%, at 95% confidence limits.

3. Results and discussion

Table 1 lists the experimental Krytox® densities as function of temperature and pressure obtained in this study. Fig. 2 shows the change in Krytox® density as a function of pressure to 275 MPa at different temperatures. The density of Krytox® GPL 102 ranges from 1622 to 2164 kg m^{-3} in the temperature and pressure range investigated. These Krytox® densities are approximately twice as large as the densities of common lubricants such as paraffinic, naphthenic, and polyol ester lubricants, at similar conditions [30,32]. However, Krytox® densities are similar to those reported for Demnum®, a linear PFPE lubricant (shown here) [30]. The Demnum® data are only reported at a limited range of