Vapor Pressure, Density, Viscosity, and Surface Tension of Tetrapropylene Glycol

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ABSTRACT: The properties of 2-(2-[2-(2-hydroxypropoxy)-propoxy]propoxy)propan-1-ol (tetrapropylene glycol, TePG) were measured as a function of temperature: vapor pressure (409.85 to 582.15) K, density (298.15 to 443.15) K, viscosity (288.15 to 393.15) K, and surface tension (298.15 to 468.15) K. The obtained data for tetrapropylene glycol were regressed using correlations from simulation software. We are developing a new industrial process to separate propylene glycols mixtures, obtained via the hydrolysis of 1,2-epoxy propane. One component of the mixture is not defined in the database of the simulation program. For synthesis and simulation of this process, it is necessary to have (1) the component TePG defined as a chemical structure, (2) the physical and transport properties of this component, and (3) vapor–liquid equilibrium data for the components of the mixture.

1. INTRODUCTION

A mixture of propylene glycol oligomers is obtained under elevated temperature and pressure by hydrolysis of 1,2-epoxy propane (propylene oxide, PO), a chemical intermediate whose global consumption exceeds 4.5 million tones/year.1 This mixture is separated by distillation, to produce 1,2-propanediol (monopropylene glycol, further abbreviated as MPG) + 1-(2-hydroxypropoxy)propan-2-ol (dipropylene glycol, further abbreviated as DPG) + 2-(2-hydroxypropoxy)propan-1-ol (tripropylene glycol, further abbreviated as TPG) + 2,2-(2-hydroxypropoxy)propan-1-ol (tetrapropylene glycol, further abbreviated as TePG) available in the literature4 and with several experimental data sets determined for tripropylene glycol. Figure 1 shows the chemical structures for monopropylene glycol, dipropylene glycol, tripropylene glycol, and tetrapropylene glycol.

2. EXPERIMENTAL SECTION

2.1. Materials. Tetrapropylene glycol used for the experimental determination of physical and transport properties is obtained from a mixture of higher propylene glycols available from Dow Chemical Company. This mixture contains 0.98 mass fraction TPG and TePG according to the certificate of analysis.

Received: January 23, 2013
Accepted: September 26, 2013
Published: October 8, 2013
identification of TePG isomers, we decided to use in our experimental measurements a mixture of the isomers in the proportion resulting from reaction. Further we will use the nomenclature tetrapropylene glycol or the abbreviation TePG for the isomers mixture with molar mass 250 g·mol⁻¹, normal boiling temperature experimentally determined 582.2 K, and chemical formula C₁₂H₂₆O₅. Descriptions of the TePG and TPG (also used in experiment) samples are presented in the Table 1.

The pressure was measured using a DPI 705 sensor with the measuring range between 0 and 1.01·10⁵ Pa and the temperature was measured with VWR International, LLC, NIST traceable digital thermometers (±0.05 % accuracy and 0.001 K resolution).

2.2. Apparatus and Procedure. Tetrapropylene glycol vapor pressure is experimentally determined using a total pressure apparatus built in our laboratory. This static apparatus of our laboratory is shown schematically in Figure 3. In this figure the numbers in brackets represent the parts of the apparatus. A sample of TePG (5) is introduced into the equilibrium cell (4). The cell is connected to a U-shaped tube (6) containing a manometric liquid, mercury. The degassing of the sample using liquid nitrogen and a vacuum pump was a standard procedure, before the vapor pressure measurement. The solution was frozen near the liquid nitrogen temperature, and degassed using the vacuum pump to remove any gaseous impurities for 20 min. This step was performed when coupling valve (8) was open. After degassing, coupling valve (8) is closed and the equilibrium cell and the U-shaped tube are placed in transparent glass-walled bath (1) with thermostatic oil (2), where the desired temperature was maintained within ±0.05 K. By heating the TePG sample, vapors are emitted that cause the oscillation of the level in the U-shaped tube. When level of the mercury remains constant (pressure of the system did not change for 30 min), air is introduced in the system through a valve (16) until the level of the mercury in the tube is the same in the two branches as it can be seen on a graduated scale (7). At this point the vapor pressure and temperature are measured, respectively, using a pressure sensor (12) and digital pressure indicator (13) and a temperature sensor (10) and digital thermometer (11). Three replicates were performed for each state condition. The standard uncertainty for temperature was ±0.01 K and the relative standard uncertainty for vapor pressure was 0.01.

Densities of TePG are measured using a calibrated glass pycnometer having a bulb volume of 10 cm³. The volume of the pycnometer was calibrated as a function of temperature using distilled, deionized, and degassed water at various temperatures. The pycnometer filled with liquid was kept in a thermostatically controlled oil bath (maintained constant to ±0.05 K) for (20 to 25) min to reach thermal equilibrium. The density measure-
ments were carried out at various temperatures. Each experimental density value was an average of at least three measurements. The estimated uncertainties\(^6\) for temperature and density were ± 0.01 K and ± 0.14 kg m\(^{-3}\), respectively.

The liquid dynamic viscosity of TePG (\(\eta\)) was obtained by multiplying the experimental determined kinematic viscosity (\(\nu\)) by the measured density (\(\rho\)). The kinematic viscosity of TePG was performed with two commercial capillary viscometers of Ubbelohde type which have capillary diameters of 0.78 mm and 0.88 mm.\(^2\) Double distilled, deionized, and degassed water was used for the calibration.\(^10\) The flow time was determined with a digital stopwatch capable of measuring time within ± 0.01 s. Measurements were accomplished in transparent glass-walled water and glycerin baths, depending on the desired temperature, with a thermal stability of ± 0.01 K. Each measurement was repeated at least five times, and the results were averaged. The kinematic viscosity (\(\nu\)) was calculated from the following equation:

\[
\nu = k \cdot t
\]

where \(\nu\) is the kinematic viscosity, \(t\) is the flow time of the liquid in the viscometer, and \(k\) is the calibration viscometer constants provided by the manufacturer that has values of 0.1193 for range of temperature (288.15 to 333.15) K and 0.02853 for range (338.15 to 393.15) K. The relative standard uncertainty\(^6\) for dynamic viscosity was 0.01.

Surface tension of TePG was determined using a Traube stalagmometer by drop method, where the number of drops of the liquid and water were measured at constant temperature.\(^11\) The measurements were done in three replicates, and the average values are reported. We estimate the uncertainties\(^6\) in our measurements to be within ± 0.01 K for temperature and ± 0.0001 N m\(^{-1}\) for surface tension.

### 3. RESULTS AND DISCUSSION

Experimental data for TePG properties were regressed using the most appropriate correlation of simulation software. Correlations of experimental data used in regression were chosen taking into account the correlations available in the simulation software for MPG, DPG, and TPG properties.\(^4\)

#### 3.1. Vapor Pressure

The results for the vapor pressure measurements of tetrapropylene glycol for temperatures from (409.85 to 582.15) K are presented in Table 2. The vapor pressure of tetrapropylene glycol was measured at higher temperatures, compared to other properties presented, because at lower temperatures than these the vapor pressure has very low values and is very difficult to obtain. The vapor pressure experimental data were regressed. In Figure 4 are presented the relative deviations \(\Delta p/p\) between the calculated vapor pressures \(p(\text{calc})\) and those experimentally determined \(p(\text{expt})\). Equation 2 represents the specific correlation for vapor pressure of TePG as function of temperature written with the values of the coefficients obtained from the experimental data regression.

\[
\ln(p/\text{kPa}) = 1.7975 \times 10^5 - \frac{6.4082 \times 10^6}{T} - 28739 \ln T + 0.079537 T^{-2} - 6.7778 \times 10^{-5} T^{-3}
\]

Furthermore, we obtained additional experimental points for TPG vapor pressure for comparison with PRO II database.\(^4\) Thus, our experimental procedure and the apparatus for the vapor pressure measurements was verified. The experimental vapor pressures and vapor pressure curve traced with eq 2 of TePG, the experimental points of TPG, and vapor pressure curves for others propylene glycols as MPG, DPG, and TPG from PRO II database,\(^4\) are presented in the Figure 5. The vapor pressure of propylene glycols increases with the increase in temperature and decreases with increase in molar mass at fixed temperature. The low vapor pressures of propylene glycols compared with those of water, situate the propylene glycols in the class of high boiling point liquids. The low volatility of propylene glycols reduces their tendency to evaporate and leads to their use as plasticizers, antifreeze, and bygrosopic agents.

#### 3.2. Density

Table 3 contains experimental values of densities for tetrapropylene glycol determined in the range from (298.15 to 443.15) K. After the experimental data regression, according to PRO II software, the relative deviations \(\Delta \rho/\rho\) of the calculated liquid densities \(\rho(\text{calc})\) from those determined experimentally \(\rho(\text{expt})\) were determined and are presented in Figure 6. The specific correlation of tetrapropylene glycol density as function of temperature is given by eq 3.

\[
\rho/\text{kg m}^{-3} = 1041.2 - 1.3992 \cdot T + 0.036660 \cdot T^2 - 0.00080351 \cdot T^3
\]

Figure 7 shows the DPG and the TPG curves of densities as function of temperature, data available in PRO II database, in comparison with a few experimental points of TPG density and

| Table 2. Experimental Values of Vapor Pressure \(p\) for Tetrapropylene Glycol at Different Temperatures \(T\*) |
|----------------|----------------|----------------|----------------|
| \(T/\text{K}\) | \(p/\text{kPa}\) | \(T/\text{K}\) | \(p/\text{kPa}\) |
| 409.85 | 0.01 | 537.15 | 32.05 |
| 462.55 | 2.68 | 543.15 | 37.42 |
| 480.15 | 5.34 | 545.15 | 40.02 |
| 486.15 | 6.66 | 550.15 | 45.37 |
| 492.15 | 8.02 | 554.15 | 50.69 |
| 500.15 | 10.72 | 556.15 | 53.36 |
| 507.15 | 13.36 | 560.15 | 58.74 |
| 513.15 | 16.05 | 564.15 | 64.02 |
| 518.15 | 18.79 | 567.15 | 69.28 |
| 522.15 | 21.34 | 570.15 | 74.63 |
| 527.15 | 24.02 | 575.15 | 83.34 |
| 530.15 | 26.71 | 582.15 | 101.02 |

\(*u(T) = 0.01 \text{ K and relative standard uncertainty } u(\rho) = 0.01.\)
with experimental and calculated values of TePG density. As it can be seen in this figure the density decreases with the increase in temperature for propylene glycols and increases with the increase in molar mass at fixed temperature. At a constant temperature, it can be observed that the differences in density between these three propylene glycols are roughly equal. This is due to the difference of chemical structure of DPG, TPG, and TePG, more specifically assignment of a propoxy group in this homologue series.

### 3.3. Viscosity.

Table 4 contains the experimental values of viscosities of tetrapropylene glycol determined in the range from (288.15 to 393.15) K. Figure 8 shows the relative deviations $\Delta \eta/\eta$ of the liquid dynamic viscosities $\eta$ (calc) calculated with eq 4 as a function of temperature from those experimentally determined $\eta$ (expt).

$\eta = -2.2932 \times 10^{-5} + 5.6583 \times 10^{-6}/T + 39443 \ln T$

$$-0.26295 \cdot T^2 + 0.00034739 \cdot T^3$$

(4)

Experimental and calculated data sets of TePG viscosities are compared with viscosities data sets for DPG and TPG available in the literature and with several experimental values for TPG (Figure 9). For temperatures less than 310 K the dynamic viscosities are different, for temperatures from (315 to 350) K the TePG dynamic viscosity values are roughly equal to TPG.
viscosity values. For temperatures greater than 370 K all the three glycols have almost the same dynamic viscosities. This property is not influenced by the number of propoxy groups existing in the chemical structure of propylene glycol. Propylene glycols flow freely at high temperatures, while at low temperatures their viscosities increase until they eventually set and fail to flow. The variation of viscosity with temperature is necessary for pumping and piping calculations.2

3.4. Surface Tension. The experimental surface tension values of tetrapropylene glycol ranging from (298.15 to 468.15) K are reported in Table 5. The data were regressed and the specific correlation of TePG surface tension as a function of temperature was obtained (eq 5). The relative deviations $\Delta \sigma/\sigma = (\sigma(\text{calc}) - \sigma(\text{expt}))/\sigma(\text{calc})$ from those determined experimentally $\sigma(\text{expt})$ are presented in Figure 10.

$$\sigma = 0.036355 - 8.2573 \cdot 10^{-5} \cdot T$$  \hfill (5)

The surface tension of dipropylene, tripropylene, and tetrapropylene glycols against temperature is given in Figure 11. It can be seen that the surface tension decreases with the increase in temperature and increases with the increase in molar mass at fixed temperature for propylene glycols. The variation of surface tension of these propylene glycols with temperature is quasi-linear in the temperature range (298.15 to 468.15) K. Surface tension differences between propylene glycols presented are uniform due to the presence of a new propoxy group in the chemical structure of the respective glycol. Surface tension is an important property when the wetting or penetrating ability of a liquid is considered. Surface tensions of propylene glycols are lower than those of water.2

The temperature range for experimental data of liquid density, liquid dynamic viscosity, and surface tension was from (288.15 to 468.15) K, because these are the temperature limits of the new industrial process to separate the propylene glycols mixture that we are developing.

4. CONCLUSIONS

In this work we presented experimental data for vapor pressure ranging from (409.85 to 582.15) K, the liquid density ranging from (298.15 to 443.15) K, the liquid dynamic viscosity ranging from (288.15 to 393.15) K, and the surface tension ranging from

Table 5. Experimental Values of Surface Tension $\sigma$ at Temperature $T$ and Pressure $p = 0.1$ MPa for Tetrapropylene Glycol$^a$

| $T$/K   | $\sigma$/N·m$^{-1}$ |
|---------|---------------------|
| 298.15  | 0.0343              |
| 308.15  | 0.0334              |
| 318.15  | 0.0326              |
| 328.15  | 0.0318              |
| 348.15  | 0.0302              |
| 368.15  | 0.0285              |
| 378.15  | 0.0277              |
| 398.15  | 0.0261              |
| 408.15  | 0.0252              |
| 418.15  | 0.0244              |
| 428.15  | 0.0236              |
| 438.15  | 0.0227              |
| 448.15  | 0.0219              |
| 458.15  | 0.0211              |
| 468.15  | 0.0202              |

$^a$Standard uncertainties $u$ are $u(T) = 0.01$ K, $u(p) = 10$ kPa, and the combined expanded uncertainty $U_C$ is $U_C(\sigma) = 0.0001$ N·m$^{-1}$ (0.95 level of confidence).

Figure 8. Relative deviations $\Delta \eta/\eta = (\eta(\text{calc}) - \eta(\text{expt}))/\eta(\text{calc})$ of the calculated liquid dynamic viscosities with eq 4 $\eta(\text{calc})$ as a function of temperature from those determined experimentally $\eta(\text{expt})$ for tetrapropylene glycol.

Figure 9. Variation of liquid dynamic viscosities $\eta$ with temperature $T$ for higher propylene glycols: $\cdots$, dipropylene glycol from PRO II database; $\cdots$, tripropylene glycol from PRO II database; $\bigcirc$, experimental liquid dynamic viscosity of TPG; $\Box$, experimental liquid dynamic viscosity of TePG; $\bigcirc$, liquid dynamic viscosity curve for TePG traced with regress eq 4.

Figure 10. Relative deviations $\Delta \sigma/\sigma = (\sigma(\text{calc}) - \sigma(\text{expt}))/\sigma(\text{calc})$ of the calculated surface tension with eq 5 $\sigma(\text{calc})$ as a function of temperature from those determined experimentally $\sigma(\text{expt})$ for tetrapropylene glycol.
K of tetrapropylene glycol. Our physical and transport properties measurements of tetrapropylene glycol were correlated as functions of temperature. The obtained correlations of the TePG properties present the next maximum relative deviations: 1.72% for vapor pressure, 0.0384% for density, 0.712% for dynamic viscosity, and 0.262% for surface tension. Furthermore, the tetrapropylene glycol properties reported in this study are sufficiently accurate for the design of a new industrial process for obtaining TePG from a glycols mixture.

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**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The authors would like to thank Dow Chemical Company for sample material and Mr. Alexandru Pană, Head of Quality Control Department, S. C. Oltchim S. A. Râmnicu Vâlcea, Romania, for technical assistance.

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**Figure 11.** Variation of surface tension $\sigma$ with temperature $T$ for higher propylene glycols: $\cdots$, dipropylene glycol from PRO II database; $-\cdots-\cdots$, tripropylene glycol from PRO II database; $\bullet$, experimental surface tension of TPG; $\square$, experimental surface tension of TePG; $\implies$, surface tension curve for TePG traced with regress eq 5.