New measurements and modeling of high pressure thermodynamic properties of glycols

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Abstract

New experimental density data of six glycols, namely ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TriEG), tetraethylene glycol (TeEG), pentaethylene glycol (PeEG) and hexaethylene glycol (HeEG) were determined in a wide range of temperatures (283–363 K) and pressures (0.1–95 MPa). The experimental density data was first correlated, as function of temperature and pressure, using the modified Tait-Tammann equation, and the derivative properties, such as isobaric thermal expansion coefficients and the isothermal compressibility, were estimated. It is shown that the isobaric thermal expansivity converges to a cross-over point that, although commonly observed for non-associating compounds, is here reported for the first time for the studied glycols. This denotes the presence of hydrogen bonds, mainly dominated by dispersive interactions, breaking and decreasing intermolecular interactions as the temperature and the number of glycols ethoxy groups increase.

The study is completed with the modeling of the experimental data using the soft-SAFT equation of state. A molecular model, considering the glycol molecules as LJ chains with one associating site at each of the compounds’ end groups (hydroxyl groups) is proposed for all the glycols, allowing the EoS to provide an excellent description of the glycols’ pVT surface. Additionally, the optimized parameters were correlated with the compound’s molecular weight, providing a good prediction of the PEG400 density and the compounds’ derivative properties.

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1. Introduction

Ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TriEG), tetraethylene glycol (TeEG), pentaethylene glycol (PeEG) and hexaethylene glycol (HeEG) are the first six members of the homologous series of polyethylene glycols commonly used as raw materials in a large number of industrial applications. Glycols are common reactants and intermediates in a wide range of reactions of aldehydes, alkyl halides, amines, azides, carboxylic acids, ethers, mercaptans, nitrate esters, nitriles, nitrite esters, organic esters, peroxides, phosphate esters, sulfate esters and in resin formation (including the condensation with dimethyl terephthalate or terephthalic acid resulting in a polyester resin) [1,2]. Consequently, glycols physical properties stand, as extremely relevant for the development of new technologies and the enhancement/optimization of existent processes. Process development and optimization usually relies on process simulators that require an accurate description of the compounds’ thermophysical properties, which for the case of glycols are not fully and accurately characterized. Furthermore, these process simulators depend on correlations and equations of state (EoSs) that, in turn, require for their development or parameterization, an accurate thermophysical data characterization of the target compounds.

Soft-SAFT (Statistical Associating Fluid Theory) EoS ability to
consistently describe the phase equilibrium and thermophysical properties of a large number of compounds, using a set of transferable molecular parameters built from the pure compounds properties, make soft-SAFT as the most outstanding thermodynamic model for the description of polar and associative compounds [3,4] in a wide range of pressures and temperatures conditions [5]. Soft-SAFT EoS, as any molecular-based EoS, relies on the proper selection of a strong coarse-grained model capable of representing the basic physical features of the compounds to be described.

Recent developments on SAFT-type EoSs, have emphasized the importance to adjust the EoS molecular parameters against properties affected by association, aiming to obtain a realistic balance between dispersive and associative energies [6]. Although the selection of the most reliable properties for the EoS optimal parameterization is still under discussion, the simultaneous description of the density and its pressure and temperature derivatives appear as the most relevant [7].

In the continuation of a previous work [8] aiming at the accurate thermophysical characterization of glycols, the density as function of pressure (up to 95 MPa) and temperature (283–363) K was investigated for the first four members of the series of glycols. Apart from the characterization of their properties, the selected set of compounds allows investigating the combined effects of pressure and the chain length, i.e. the number of ether groups on the compounds’ density and other derivative thermodynamic properties. Additionally, a new soft-SAFT EoS molecular model and optimized molecular parameters are proposed here to model the reported experimental data. Based on the physical trends, the optimized molecular parameters were correlated with the glycols’ molecular weight, as previously done with other compounds [9]. This approach was validated by using the soft-SAFT EoS parameters obtained from these correlations to predict the polyethileneglycol (PEG 400) high pressure density data and the compounds’ derivative properties with success.

2. Experimental section

2.1. Materials

Experimental densities were measured for six glycols, namely ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TriEG), tetraethylene glycol (TeEG), pentaethylene glycol (PeEG), hexaethylene glycol (HeEG), and for the polyethylene glycol (PEG 400) on the (283–363) K temperature range and (0.1–95) MPa pressure range. The compounds were acquired from Sigma Aldrich (DEG, TriEG, TeEG and PEG 400) and Acros Organics (PeEG and HeEG), with mass fraction purities higher than 99% (Fluka and Sigma Aldrich compounds) and 98% (Acros Organics compounds).

To remove traces of water and volatile compounds, individual samples of each glycol were dried at moderate temperature (≈323 K), vacuum (≈0.1 Pa) and under continuous stirring, for a minimum of 48 h prior to the measurements. The purity of each glycol was checked by 1H and 13C NMR, both before and after the measurements, to assure that no degradation occurred. The final water content, after the drying step and immediately before the measurements, was determined with a Metromh 831 Karl Fischer coulometer (using the Hydranal - Coulomat AG from Riedel-de Haén as analyte). The full name, chemical structure, CAS number, molecular weight, average water content, mass purity and supplier of each glycol are reported in Table 1.

2.2. Density measurements

Densities were measured in the (283–363) K temperature and (0.1–95) MPa pressure ranges using a DMA-HPM, coupled with a mPDS 5 unit, high pressure densimeter from Anton Paar. The measuring cell was thermostated by circulating a heat-carrier fluid thermo-regulated, with a temperature stability of ±0.01 K, by means of a thermostat bath circulator (Julabo MC); the standard uncertainty on the temperature was found to be 0.1 K. The pressure was measured by a piezoresistive silicon pressure transducer (Kulite HEM 375) with an accuracy better than 0.2%. The transducer was fixed directly in the \(\%\) stainless steel line, to reduce dead volumes, and placed between the DMA-HPM measuring cell and a movable piston.

The densimeter was calibrated with ultra-pure water (double-distilled, passed through a reverse osmosis system, and further treated with a Milli-Q plus 185 water purification apparatus. It had a resistivity of 18.2 MΩ cm and a total organic carbon smaller than 5 μg L\(^{-1}\), being free of particles greater than 0.22 μm), toluene (acquired from Sigma Aldrich, with a mass fraction purity higher than 99.8%) and dichloromethane (acquired from AnalR NOR-MAPUR, with a mass fraction purity higher than 99.9%) in the (283–363) K, (0.1–100) MPa and (0.810–1.377) g cm\(^{-3}\) temperature, pressure and density ranges, respectively. The polynomial suggested by the manufacturer, Eq. (1), was adopted to calculate the density of the sample, within the above mentioned adjustment range, from the period of oscillation

\[
\rho = A_1 + A_2 \cdot T + A_3 \cdot p + A_4 \cdot T^2 + A_5 \cdot p^2 + (A_6 + A_7 \cdot T + A_8 \cdot p + A_9 \cdot T^2 + A_{10} \cdot p^2) \cdot period^2 + A_{11} \cdot period^4
\]

where \(T\) is the temperature, \(p\) the pressure, period the oscillation period and \(A_i\) (with \(i = 1 \ldots 11\)) the polynomial coefficients. A percentage absolute average deviation (%AAD) of 0.08% and relative deviation (\(\Delta\rho\)) of 1.2 \(\cdot\) 10\(^{-4}\) g cm\(^{-3}\) were obtained towards the calibration compounds’ density data available in the literature. The standard uncertainty on the density (\(u(\rho)\)) was found to be 5 \(\cdot\) 10\(^{-4}\) g cm\(^{-3}\).

The viscosity influence on the density uncertainty, due to damping effects on the vibrating tube, can be evaluated by means of the following equation provided by Anton Paar:

\[
\Delta\rho = \rho \cdot \left(-0.5 + 0.45\eta^{1/2}\right) \cdot 10^{-4}
\]

where \(\rho\), \(\Delta\rho\) and \(\eta\) represent the density obtained, the difference between the obtained and corrected density and the compound viscosity (in mPa.s). It is well known that for viscosities lower than 100 mPa.s the viscosity has little to no impact on the density determination. In fact, corrections as high as 2 \(\cdot\) 10\(^{-4}\) g cm\(^{-3}\), were obtained making the density correction unnecessary.

3. Modeling

3.1. Thermodynamic properties

Liquid densities were correlated as function of temperature and pressure using the modified Tait-Tammann equation
The isothermal compressibility, \(k_T\), is a measure of the fraction change in size per degree change in temperature at a constant pressure and can be described by the isothermal temperature derivative of density

\[
k_T = \left( \frac{\partial \rho}{\partial p} \right)_T
\]

(7)

The isobaric thermal expansivity, \(\alpha_p\), is a measure of the fractional change in volume per degree change in temperature at a constant pressure and can be described by the isobaric temperature derivative of density

\[
\alpha_p = \left( \frac{\partial \rho}{\partial T} \right)_p
\]

(8)

### 3.2. Soft-SAFT EoS

The general expression for SAFT equations is given in terms of the residual Helmholtz free energy for a n-component mixture of associating chain molecules, and is typically expressed as the sum of three terms: a reference term \(A^{\text{ref}}\), defined as the contribution to the Helmholtz energy of the fluid due to the monomer interactions; a chain term \(A^{\text{chain}}\), that considers chain formation; and an association term \(A^{\text{assoc}}\), which explicitly takes into account short-range attractive interactions, such as hydrogen bonding.

\[
A^{\text{es}} = A^{\text{total}} - A^{\text{deal}} = A^{\text{ref}} + A^{\text{chain}} + A^{\text{assoc}}
\]

(9)

In SAFT-type EoS, the chain and association terms are based on the Wertheim’s first-order perturbation theory [10–12], while different versions vary on the choice of the reference term. The soft-SAFT EoS uses a Lennard-Jones (LJ) spherical fluid as a reference potential. The LJ reference term, that takes into account the repulsive and attractive interactions of the monomers constituting the chain, is described in our work by means of Johnson’s equation [13]. The chain and the associating terms are built from a thermodynamic perturbative approach, that contain structural information of the reference fluid \(g(r)\) as a function of density and temperature. A more detailed description of the soft-SAFT EoS terms can be found in previous publications [3,4].

#### 3.2.1. Molecular model

Being a molecular-based EoS the adequate selection of a reliable coarse-grained model, capable of representing the basic physical features of the compounds, stand as highly relevant for the accurate prediction of the systems phase equilibria and thermophysical properties. Soft-SAFT EoS relies on the pre-selection of a molecular model for the pure compounds. For non-associating molecules soft-SAFT requires three molecular parameters: the chain length \(m\), the model diameters \((\varrho)\) and the dispersive energy \(\varepsilon\). While two additional parameters, \(\varepsilon^{\text{HB}}\) and \(\varepsilon^{\text{AB}}\), are needed to take into account the association.

The soft-SAFT EoS has been used to model short glycols in a previous publication [14]. There, the glycols were considered as LJ chains with one associating site at each end group (having two association sites per molecules), with all the association interactions being equivalent, i.e. all sites have the same values for the \(\varepsilon^{\text{AB}}\) and \(\varepsilon^{\text{HB}}\) parameters, and only allowing “AB” interactions. Excellent agreement was achieved for the temperature-density diagram and vapor pressure and for the mixture calculations. In the current work, after checking the performance of the original model for derivative properties, the molecular parameters'
determination was improved by considering the compounds’ end groups (hydroxyl groups) as two different associating sites “A” and “B” (one for each hydroxyl group). We now consider the dual positive-negative nature of the hydroxyl group by allowing all kind of interactions (“AA”, “BB” and “AB”). The same associating model was used for all the studied compounds investigated in this work.

4. Results and discussion

Density measurements were carried out at temperatures ranging from (283—363) K and pressures from (0.10—95) MPa. Although density data at or near atmospheric pressure is widely available in the literature (a summary of all the literature density data at atmospheric pressure has been reported in a previous publication [8]), pVT data is scarcer. Considering that an exhaustive study, covering atmospheric pressure density data of EG, DEG, TriEG and TeEG obtained with two different equipments and methodologies has already been published [8], the density data at atmospheric pressure is only measured and included here for comparison with the data already reported [8]. As depicted in Fig. 1, a good agreement is found for all the compounds, with percentage average deviations (%AD) ranging between ±0.1%.

Several authors have reported density data as function of a wide range of pressures and temperatures for EG. Wong and Hayduk [15] have reported measurements for pressures up to 7 MPa and temperatures between (298 and 348) K, Guignon et al. [16], for pressures up to 350 MPa at 288 K, Sagdeev et al. [17], for pressures up to 245 MPa and temperatures between (293 and 464) K, and Atilhan et al. [18], for pressures up to 60 MPa and temperatures between (278 and 358) K. Fewer data are available for the rest of the glycols. For DEG and TriEG, data was reported only by Sagdeev et al. [17], for pressure up to 250 MPa and temperatures between (293—465) K. To our knowledge, pVT data for TeEG, PeEG and HeEG is reported here for the first time. Similarly to what was observed for the atmospheric pressure density data, and discussed in a previous work [8], some discrepancies between authors are observed also for density data as function of pressure. For EG percentage average deviations ranging between 0.1% and 0.2%, increasing with pressure and decreasing with the temperature, are observed against the data reported by Atilhan et al. [18], as depicted in Fig. 2.

The data here reported is in good agreement with those by Wong and Hayduk [15] and Guignon and coworkers [16], with percentage absolute average deviations of 0.05% ($\Delta \rho = 0.0006$ g cm$^{-3}$) and 0.04% ($\Delta \rho = 0.0005$ g cm$^{-3}$), respectively. Higher percentage average deviations were observed, against data reported by Sagdeev et al. [17] both for EG (0.1% to 0.4%) and DEG (0.01% to 0.7%). However, contrary to the tendency observed for the data of Atilhan et al. [18], where the temperature increase lead to a decrease on the density data deviations, the deviations against Sagdeev et al. [17] data increase with the temperature. Overall, the density data measured in this work presents small and no systematic deviations against those available in the literature.

Fig. 1. Percentage average deviations (%AD) (left) and density differences (right) between density data, at 0.1 MPa, determined here and that reported in a previous publication, for the EG, DEG, TriEG and TeEG [8].

Fig. 2. Percentage average deviations (left) and density differences (right) between literature [15—18] and experimental pVT data as function of pressure and temperature for the EG, DEG and TriEG.
The experimental pressure-volume-temperature (pVT) data obtained is depicted in Fig. 3 and reported in the Supporting information. The data were correlated using the modified Tait-Tammann and the coefficients obtained are reported in Table 2. The obtained coefficients allow a good description of the experimental pVT data with a %AD of 7.3 $\times$ 10^{-4}%, as shown in Fig. 3.

**soft-SAFT Modeling.** As mentioned in the Molecular Model subsection, soft-SAFT EoS has been used in a previous publication [14] for modeling VLE data of glycols + gas systems. Only the first members of the family were modeled in the previous work. A simple two-sites association molecular model considering the compounds as LJ chains with one “A” and one “B” sites, allowing only “AB” interactions was used for calculating the solubility data. We have used the original model and parameters to calculate the derivative properties of the compounds, namely isothermal compressibility and isobaric thermal expansivity, and have found that they were not able to adequately describe the compounds’ derivative properties. In addition, having available data for more members of the series allows assessing the model and parameters in a more robust manner. In this work, glycols are here still modeled with one associating site at each end group of the compound (hydroxyl groups) but with a higher degree of associative interactions.
Concerning the fitting of the molecular parameters, pure compounds’ vapor pressure and saturated liquid density data were used to obtain an optimal set of values. For the PeEG and HeEG, to the best of our knowledge, no vapor pressure data and saturated density data are available, making the optimal parameters determination feasible by using the pVT data measured in this work. %AAD of 0.20 where obtained for the soft-SAFT fitting against PeEG and HeEG.

As depicted in Figs. 4 and 5, the selected molecular model and optimized molecular parameters, reported in Table 3, provide an excellent description of the glycols properties, with an overall %AAD for the compounds’ vapor pressure, saturated liquid and vapor densities of 9.61, 0.28 and 9.05, respectively.

### Table 2

<table>
<thead>
<tr>
<th></th>
<th>$A_0$/kg.m$^{-3}$</th>
<th>$A_1$/kg.m$^{-1}$K$^{-1}$</th>
<th>$10^4 A_2$/kg.m$^{-1}$K$^{-2}$</th>
<th>$10^2 C$</th>
<th>$B_1$/MPa</th>
<th>$B_2$/MPa.K$^{-1}$</th>
<th>$10^3 B_3$/MPa.K$^{-2}$</th>
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<tbody>
<tr>
<td>EG</td>
<td>1279.468</td>
<td>−0.44067</td>
<td>−4.3236</td>
<td>8.4659</td>
<td>276.235</td>
<td>0.32667</td>
<td>−1.7119</td>
</tr>
<tr>
<td>DEG</td>
<td>1300.574</td>
<td>−0.53829</td>
<td>−2.9866</td>
<td>7.8985</td>
<td>380.081</td>
<td>−0.66304</td>
<td>0.012925</td>
</tr>
<tr>
<td>TriEG</td>
<td>1341.397</td>
<td>−0.70587</td>
<td>−1.2212</td>
<td>7.8605</td>
<td>500.831</td>
<td>−1.3206</td>
<td>0.88587</td>
</tr>
<tr>
<td>TeEG</td>
<td>1359.730</td>
<td>−0.80848</td>
<td>0.13374</td>
<td>7.9365</td>
<td>474.279</td>
<td>−1.1438</td>
<td>0.58836</td>
</tr>
<tr>
<td>PeEG</td>
<td>1363.834</td>
<td>−0.81493</td>
<td>0.0549</td>
<td>8.1804</td>
<td>506.3304</td>
<td>−1.3284</td>
<td>0.8964</td>
</tr>
<tr>
<td>HeEG</td>
<td>1398.292</td>
<td>−1.0183</td>
<td>3.0346</td>
<td>8.7039</td>
<td>824.9550</td>
<td>−3.0925</td>
<td>3.415</td>
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</tbody>
</table>

### Table 3

<table>
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<tr>
<th></th>
<th>$m$</th>
<th>$\sigma$ (Å)</th>
<th>$\epsilon$/$k_B$ (K)</th>
<th>$\sigma^{\text{eff}}$/$k_B$ (K)</th>
<th>$k_B H_B$ (Å$^3$)</th>
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<tbody>
<tr>
<td>EG</td>
<td>1.951</td>
<td>3.533</td>
<td>325.10</td>
<td>4140</td>
<td>2600</td>
</tr>
<tr>
<td>DEG</td>
<td>2.825</td>
<td>3.733</td>
<td>342.77</td>
<td>3891</td>
<td>2600</td>
</tr>
<tr>
<td>TriEG</td>
<td>3.525</td>
<td>3.887</td>
<td>346.18</td>
<td>3891</td>
<td>2600</td>
</tr>
<tr>
<td>TeEG</td>
<td>4.311</td>
<td>3.964</td>
<td>349.14</td>
<td>3891</td>
<td>2600</td>
</tr>
<tr>
<td>PeEG</td>
<td>5.256</td>
<td>3.970</td>
<td>351.65</td>
<td>3891</td>
<td>2600</td>
</tr>
<tr>
<td>HeEG</td>
<td>6.175</td>
<td>3.983</td>
<td>354.44</td>
<td>3891</td>
<td>2600</td>
</tr>
<tr>
<td>PEG400</td>
<td>8.321</td>
<td>4.049$^a$</td>
<td>357.47$^a$</td>
<td>3891</td>
<td>2600</td>
</tr>
</tbody>
</table>

$^a$ Molecular parameters estimated using Eqs. (10)–(12).
Furthermore, as previously done for other homologous series, the optimized molecular parameters were correlated with the compounds’ molecular weight, in order to identify linear trends that may allow the prediction of the behavior and properties of other glycols.

As depicted in Fig. 6 the soft-SAFT molecular parameters \(m, m \sigma^3\) and \(m \varepsilon/k_B\) present a linear dependency with the compounds’ molecular weight, which can be described by the following equations:

\[
m = 0.01894M_w + 0.7461 \\
m \sigma^3 = 1.38015M_w + 0.26992 \\
m \varepsilon/k_B = 6.93761M_w + 199.509
\]

The physical meaning of the soft-SAFT molecular parameters permits proposing correlations that will allow the thermodynamic

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**Fig. 6.** The soft-SAFT molecular parameters \(m, m \sigma^3\) and \(m \varepsilon/k_B\) present a linear dependency with the compounds’ molecular weight, which can be described by the following equations.

**Fig. 7.** Density as function of pressure and temperature for the EG, DEG, TriEG, TeEG, PeEG and HeEG. The solid lines represent the soft-SAFT EoS predictions of the experimental data.
properties prediction of other members of the homologous series. \( m^2 \) is directly related to the volume occupied by the molecule, while \( m_e/k_B \) refers to the energy of interaction per molecule, instead of per group, as expected, they linearly correlate with the molecular weight. The individual values of the molecular parameters vary with the particular compound and it is expected that \( \sigma \) and \( \epsilon \) tend to an asymptotic value as the chain length increases, since the effect of the end groups (associating groups) tends to become smaller and impose almost no impact on the molecule structure with the addition of new (\( \text{CH}_2 \)) groups [9].

The experimental data here reported were used to evaluate the predictive character of the soft-SAFT EoS in describing high pressure density data. As depicted in Fig. 7, soft-SAFT provides a very good description of the \( pVT \) surface of the studied compounds, with %AAD of 0.18, 0.06, 0.18, 0.20, 0.20 and 0.20 for EG, DEG, TriE, TeEG, PeEG and HeEG, respectively. No systematic degradation of the quality of the data with pressure, temperature or molecular weight was observed, highlighting the robustness of the parameters.

In order to evaluate the predictive ability of the correlations proposed for the glycols’ molecular parameters, the prediction of the \( pVT \) surface of a light polyethylene glycol (namely PEG400) was attempted. Although PEG400 is composed of a mixture of polyols of the generic formula \( \text{C}_2\text{H}_{4n} \cdot \text{O}_{n+1} \), with \( n = 8.2 \) to 9.1 and a molecular weight ranging from 380 to 420 g mol\(^{-1}\), it stands nonetheless as a suitable candidate to test the predictive capability of soft-SAFT. Hence, the molecular parameters of PEG400 were obtained from the proposed correlations, with the same association parameters that were used for all glycols. The mixture of polyols in PEG400 was treated following a pseudo-pure compound approach. The representation of PEG400 high pressure density is depicted in

![Fig. 8. Density as function of pressure and temperature for the PEG400. The solid lines represent the soft-SAFT EoS prediction of the experimental data.](image)

![Fig. 9. Molar volume as function of temperature, pressure and studied compounds.](image)
Fig. 8 and as depicted, the results are in very good agreement with the experimental data with a %AAD of 0.22%.

Molar volumes were also calculated and are depicted in Fig. 9 as a function of temperature, pressure and the studied compounds. As shown, the studied glycols present a small temperature and pressure dependency, with a slight molar volume increase with temperature and decrease with pressure. Furthermore, the impact of pressure and temperature on the molar volumes increases as the number of ethoxy groups increases.

As reported for molar volumes determined at 0.1 MPa, for the studied compounds [8], the molar volume increases with the number of ethoxy groups by 38.8 cm$^3$ mol$^{-1}$ per group.

Isothermal Compressibility and Isobaric thermal expansivity. The derivative properties of the experimental data, namely the isothermal compressibilities and isobaric thermal expansivities, were obtained from Eqs. (7) and (8). The isothermal compressibility, $k_T$, of the studied compounds, which reflect the volumetric changes with pressure at a fixed temperature is plotted in Fig. 10. A clear dependency with pressure and temperature is observed, decreasing significantly as the pressure increases and temperature decreases. As depicted in Fig. 10 soft-SAFT EoS provides a good qualitative description of the isothermal compressibilities, with the

Fig. 10. Isothermal compressibility, $k_T$, as function of pressure and temperature for the EG, DEG, TriEG, TeEG, PeEG and HeEG. The solid lines represent the soft-SAFT prediction.
description slightly degrading as the ethoxy groups increase.

The isobaric thermal expansion coefficients, $\alpha_p$, of the studied compounds, which reflect the volumetric changes with temperature at a fixed pressure, are plotted in Fig. 11 and present a similar pressure and temperature dependency. Moreover, as the number of ethoxy groups increase the temperature and pressure dependency becomes less relevant. Conversely, as the pressure increases the isobaric thermal expansivity presents a cross-over point which, although commonly observed for non-associating compounds, such as $n$-alkanes [21–23], is here reported for the first time for glycols. This behavior can be understood as a macroscopic manifestation of the association phenomenon occurring at the molecular level [6], with the temperature increase leading to hydrogen bonds breaking and thus, decreasing intermolecular interactions that become dominated by dispersive forces such as in the $n$-alkanes molecules. Postnikov and Chorążewski [24] have suggested that this behavior is due to an "anomalous volume expansion to the increasing temperature" with a structural transition of "a normal liquid with holes (loose packing) to a liquid with irregularly closed packed particles". The authors evidence that, although this

![Fig. 11. Isobaric thermal expansion, $\alpha_p$, as function of pressure and temperature for the EG, DEG, TriEG, TeEG, PeEG and HeEG. The solid lines represent the soft-SAFT prediction.](image-url)
phenomenon do not fall in the definition of a “phase transition, due to the absence of a discontinuity of the thermodynamic functions”, is seems related to the “different excitability of the inner degrees of freedom and various lengths of the minimal separation between particles with different energies/temperatures” as hypothesized by S. Randzio [25]. Furthermore, soft-SAFT EoS is able to describe correctly the property and also to predict the occurrence of the above discussed cross-over point.

5. Conclusions

Experimental density data of six glycols, namely ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, penta-ethylene glycol and hexaethylene glycol were determined in a wide range of temperatures (283–363 K) and pressures (0.1–95 MPa). Good agreement with previous data reported in the literature was obtained with percentage average deviations of −0.15%, while pVT data for the TeEG, PeEG and HeEG are here reported for the first time. Additionally, second order thermodynamic derivative properties, such as isothermal compressibility and isobaric thermal expansion coefficients were also estimated and discussed.

As the pressure increases, the isobaric thermal expansivity converges to a cross-over point that, although commonly observed for non-associating compounds, is here reported for the first time for glycols. This behavior can be assessed as a macroscopic manifestation of the association phenomenon occurring at molecular level, with the temperature increase leading to hydrogen bonds breaking and decreasing intermolecular interactions. Furthermore, this is also an indication that the hydrogen-bonded structure, mainly dominated by dispersive interactions, weakens as the glycols ethoxy groups increase.

The soft-SAFT EoS was employed as a molecular modeling tool to describe the new reported experimental data. A new molecular model was proposed, by considering glycols as LJ chains with one associating site at each hydroxyl group, allowing all possible types of interactions among them. A new set of optimized molecular parameters was determined using the pure compounds’ vapor pressure data and the saturated liquid and vapor densities for the first members of the family, while for PeEG and HeEG the new high pressure experimental data were used in the regression procedure. The optimized parameters provide an excellent description of the glycols densities and derivative properties. Furthermore, as previously done for other families of compounds, the optimized parameters were correlated with the glycols’ molecular weight, while the association parameters were kept constant for all members of the series. The soft-SAFT EoS predictive character was further evaluated by describing the glycols’ and a light polyethylene glycol (PEG 400) high pressure density data. As shown, the new modeling scheme allows a very good description of the pVT surface, with an % AAD (p in molL−1) of 0.17% for the studied glycols and 0.22% for the PEG400.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.fluid.2017.01.003.

References