



**CRISTOFE HENRIQUE GONÇALVES FONSECA** **MEDIÇÃO EXPERIMENTAL E MODELAÇÃO DAS PROPRIEDADES TERMOFÍSICAS DE GLICÓIS**

**EXPERIMENTAL MEASUREMENTS AND MODELLING OF THERMOPHYSICAL PROPERTIES OF GLYCOLS**





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MODELLING OF THERMOPHYSICAL PROPERTIES  
OF GLYCOLS**

Dissertação apresentada à Universidade de Aveiro para cumprimento dos requisitos necessários à obtenção do grau de Mestre em Engenharia Química realizada sob a orientação científica do Dr. João Manuel da Costa e Araújo Pereira Coutinho, Professor Catedrático do Departamento de Química da Universidade de Aveiro e co-orientação do Dr. Pedro Jorge Marques Carvalho, Estagiário de Pós-doutoramento do Departamento de Química da Universidade de Aveiro.

Dedico este trabalho ao meu irmão, meu tio e aos meus pais.

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## **agradecimentos**

Em primeiro lugar gostaria de agradecer ao Pedro Carvalho, por me ter apresentado o excelente grupo de investigação PATH, Agradeço toda disponibilidade, acompanhamento e ajuda em todo o trabalho experimental e teórico, mas também por toda amizade, apoio e preocupação.

Agradeço também a Mariana, que foi uma pessoa muito paciente e que me deu muito apoio na parte da modelação deste trabalho.

Ao Professor João Coutinho, pela possibilidade de ter realizado a minha tese mestrado sobre sua orientação, no qual agradeço a sua preocupação, confiança e os conselhos depositados no meu trabalho.

Aos meus pais pela possibilidade que me deram em tirar um curso superior e que sempre me apoiaram em tudo.

Aos meus inesquecíveis colegas de curso Sérgio Santos, Ana Arêde, Ana Patrícia Martins, Marta Reinas, aos meus colegas de casa Saulo e João por toda a boa disposição, animação e entreaajuda, mas sobretudo à Joana Cordeiro que me apoio em todo o percurso deste trabalho.

A todas pessoas do grupo PATH, no qual adorei fazer parte onde aprendi a conhecer o ambiente e o trabalho de um verdadeiro investigador. Obrigado por todos os jantares, lanches risadas e novas amizades criadas.

Um grande obrigado!

## palavras-chave

Glicóis, medição experimental, modulação, propriedades termofísicas, Equação de Estado soft-SAFT, densidade, viscosidade, capacidade calorífica, índice de refração, método de contribuição de grupo.

## resumo

Apesar da sua grande importância e necessidade nos diferentes setores industriais, verifica-se ainda um déficit significativo de dados fidedignos relativos às propriedades termofísicas de glicóis para uma ampla gama de temperaturas e pressões. Este trabalho tem como objetivo superar essa lacuna, avaliando as propriedades termofísicas de glicóis e *glymes*. Para tal, as medições experimentais de densidade, viscosidade e do índice de refração foram realizadas na gama de temperaturas (288,15-373,15) K e à pressão atmosférica. Relativamente ao conjunto de compostos estudados, juntamente com os dados disponíveis na literatura, os dados obtidos experimentalmente permitiram avaliar o efeito da estrutura molecular dos compostos nas propriedades em estudo, nomeadamente, o tamanho da cadeia, o número de grupos funcionais e o efeito da substituição dos grupos terminais.

A segunda parte do trabalho focou-se na otimização de modelos teóricos, com a finalidade de descrever as propriedades termofísicas da família de compostos em estudo. A Equação de Estado do tipo SAFT, nomeadamente a soft-SAFT EoS, foi aplicada na descrição dos dados experimentais. Novos parâmetros moleculares foram encontrados, ajustando a pressão de vapor e densidade de cada composto aos dados propostos pelo soft-SAFT. Para além de o modelo possibilitar descrever os dados obtidos experimentalmente, permite ainda estimar/prever outras propriedades, como viscosidade, capacidade calorífica e, com baixos desvios. Posteriormente, foi utilizada uma nova abordagem de ajuste dos parâmetros moleculares, tendo-se recorrido a um vasto conjunto de propriedades, de modo a garantir uma melhor descrição de sistemas mais complexos.

Finalmente, reconhecendo a importância dos métodos preditivos simples, realizou-se uma estimativa das propriedades termofísicas, recorrendo a um modelo de contribuição de grupos, proposto por Ruzika e colaboradores, bem como uma avaliação da sua aplicabilidade para os glicóis em estudo.

Em suma, a presente tese permitiu dar resposta à procura contínua das propriedades termofísicas dos compostos em estudo, fornecendo simultaneamente, novos conhecimentos acerca do impacto da estrutura molecular dos mesmos nas suas propriedades termofísicas.

**keywords**

Glycols, experimental measurements, modeling, thermophysical properties, soft-SAFT Equation of State, density, viscosity, refractive index, heat capacity, group contribution method.

**abstract**

Despite the interest from different industrial sectors, there is still a lack of quality data for glycol's thermophysical properties for a wide range of temperatures and pressures. This work aims at overcoming that requirement by evaluating the thermophysical properties of glycols and glymes. Thus, experimental measurements of density, viscosity and refractive index were carried out in the (288.15-373.15) K temperature range and at atmospheric pressure. The set of compounds studied and the data measured, alongside that available in the literature, allowed to evaluate the effect of the compounds molecular structure, like chain size, number of functional groups and the effect of changing the terminal groups, on the properties studied.

On a second part of the work the optimization of theoretical models, to describe this family of compounds, was pursued. A SAFT-type Equation of State, namely soft-SAFT EoS, was employed on the description of the experimental data. New molecular parameters, fitted against the compound's vapour pressure, density and heat capacity, are here proposed allowing soft-SAFT not only to describe the experimental data measured but predict other properties, like viscosity, heat capacity and high pressure densities with low deviations. A novel approach of fitting the molecular parameters against a wide set of properties assures a better description for more complex systems.

Recognizing the importance of simple methods, on the estimation of thermophysical properties, a group contribution model, proposed by Růžička and Domalski and by Zábanský and Růžička, was also evaluated for the glycol based compounds.

In short, this thesis narrows the gap for the continuous demanding of thermophysical properties while provides new insights on the impact of the compound's molecular structure on the thermophysical properties

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## Nomenclature

### List of symbols

$a_i$	Adjustable parameter of Růžička et al. <sup>[1,2]</sup> group contribution method
$A^{assoc}$	Helmholtz energy association term
$A^{chain}$	Helmholtz energy chain term
$A^{ideal}$	Helmholtz energy for ideal fluid
$A^{polar}$	Helmholtz energy polar contribution term
$A^{ref}$	Reference term for Helmholtz free energy
$A^{res}$	Residual Helmholtz free energy
$b_i$	Adjustable parameter of Růžička et al. <sup>[1,2]</sup> group contribution method
$B$	free-volume overlap among the molecular parameter
$C_p^{res}$	Isobaric residual heat capacity
$C_v$	Isochoric residual heat capacity
$d_i$	Adjustable parameter of Růžička et al. <sup>[1,2]</sup> group contribution method
$f_i$	soft-SAFT objective function
$f_v$	Free-volume factor
$g_{LJ}$	Radial distribution function for a fluid of LJ spheres
$k_B$	Boltzmann's constant
$k_{HB}$	Association site volume
$k_S$	Isotropic compressibility coefficient
$k_T$	Isothermal compressibility coefficient
$l_v$	Length viscosity parameter
$m$	Number of segments
$m_i$	Mass of component $i$
$M_i$	Number of association sites in component $i$
$M_w$	Molecular weight
$n_D$	Refractive index
$n_i$	number of units of type $i$
$N$	Number of points
$p$	Pressure
$p_i^{calc}$	Vapour pressure calculated by Soft-SAFT corresponding to the experimental point $i$
$p_i^{exp}$	Experimental vapour pressure corresponding to the point $i$
$p^{sat}$	Vapour pressure
$Q$	Quadrupole moment
$T$	Temperature
$T_c$	Critical temperature
$T_i^{exp}$	Temperature corresponding to the experimental point $i$
$T_{max}$	Maximum temperature
$T_{min}$	Minimum temperature
$T_r$	Reduced temperature
$R$	Universal constant of gases
$u$	Speed of sound

$x_i$	Molar fraction of component $i$
$X_i^\alpha$	Mole fraction of molecules of components $i$ nonbonded at site $\alpha$
$z$	Studied property

### Greek Letters

$\alpha$	Barrier energy viscosity parameters
$\alpha_p$	Thermal expansion coefficient
$\Delta\eta_c$	Dense-state correction term
$\Delta z$	Difference between experimental data and calculated properties by soft-SAFT ( $z^{exp} - z^{calc}$ )
$\epsilon/k_B$	Dispersive energy between segments forming the chain
$\epsilon^{HB}/k_B$	Association site energy
$\eta$	Viscosity
$\eta_0$	Viscosity of a dilute gas
$\mu$	Chemical potential
$\mu_{i,liq}^{calc}$	Chemical potential of liquid phase calculated by the soft-SAFT
$\mu_{i,vap}^{calc}$	Chemical potential of vapour phase calculated by the soft-SAFT
$\mu_{JT}$	Joules-Thomson coefficient
$\rho$	Density
$\rho_i^{exp}$	Molar density corresponding to the experimental data point $i$
$\rho_i^{calc}$	Molar density calculated by soft-SAFT EoS corresponding to the experimental data point $i$
$\rho^{liq}$	Liquid phase molar density
$\rho^{vap}$	Vapour phase molar density
$\sigma$	Segment size
$\omega$	Acentric factor

### List of Abbreviations

%AAD	Percentage average absolute deviations $\frac{1}{N} \sum_{i=1}^N \frac{ z^{exp} - z^{calc} }{z^{exp}} \times 100$
%RD	Percentage relative deviations $\frac{z^{exp} - z^{lit}}{z^{lit}} \times 100$
CH <sub>3</sub>	Methyl group
C <sub>2</sub> H <sub>5</sub>	Ethyl group
C <sub>2</sub> H <sub>5</sub> O	Ethoxy group
CPA	Cubic Plus Association
DEG	Diethylene glycol
DEGDDE	Diethylene glycol diethyl ether
DEGDME	Diethylene glycol dimethyl ether
DEGME	Diethylene glycol methyl ether
DEGMEE	Diethylene glycol mono ethyl ether
EG	Ethylene glycol
EGMEE	Ethylene glycol monoethyl ether
EoS	Equation of State
FVT	Free Volume-Theory

GC	Group contribution method
LJ	Lennard Jones fluids
PR	Peng-Robinson
NRTL	Non-random two-liquid model
OH	Hydroxyl group
TetraEG	Tetraethylene glycol
TetraEGDME	Tetraethylene glycol dimethyl ether
TriEG	Triethylene glycol
TriEGDME	Triethylene glycol dimethyl ether
SAFT	Statistical associating fluid theory
SRK	Soave-Redlich-Kwong
UNIFAC	Universal Function group Activity Coefficient
UNIQUAC	Universal quasi-chemical theory



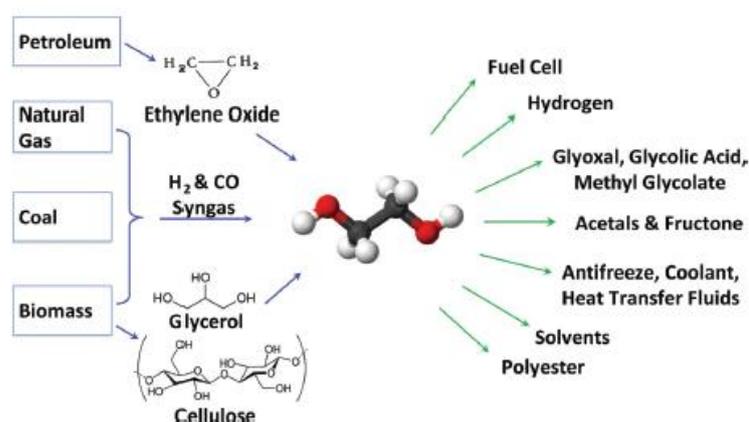
# 1. General Introduction



## 1.1 General Context

Due to the constant development of new technologies and the demand of new products, a continuous optimization of existent processes is of extreme relevance. This development and optimization relies on the accurate knowledge of the thermophysical properties of the compounds of interest<sup>[3-5]</sup>.

One of the sectors with the most prominent development is that of polymers, due to the society demand for polymeric-based products. Within the polymer industry diversity, that based on glycols and glymes stands out mostly due to its end products, like PET, polyesters fibers, antifreeze and films<sup>[6,7]</sup>. The most common glycols (diols), linear compounds with hydroxyl (-OH) groups as the terminal groups, are the ethylene glycol, di- tri- and tetraethylene glycol. Among those, the best known and most used in the industry is ethylene glycol (EG), also called 1,2-ethane diol. EG is a monomer or precursor for a larger number of glycols and mainly used as automotive engine antifreeze/coolants. Glycols are also widely used in the manufacture of polyester fibers and films. Their hygroscopicity makes them useful as conditioning agent in adhesives, cork, vinyl floor tiles, synthetic rubber, cellulose sponges, printing inks and paper products, or raw material of polyester fibers<sup>[4]</sup>. The use of EG or their oligomers, like diethylene glycol (DEG) triethylene glycol (triEG) or tetraethylene glycol (tetraEG) has been rising in the petroleum industry as an inhibitor of the formation of gas hydrate, mainly due to their low vapour pressure and their high solubility in water. TriEG is also highly used as solvent for selective removal of aromatic hydrocarbon from naphtha<sup>[8,9]</sup>.



**Figure 1.1.1-** Sources and application of ethylene glycol presented in the review by Hairong et al.<sup>[7]</sup>

Glymes, also known as glycol diethers, are a saturated polyether containing no other functional groups (i.e. OH) that present a set of interesting properties, such as completely miscibility in water and hydrocarbon solvent, liquid in a wide range of temperatures, low

## 1. General Introduction

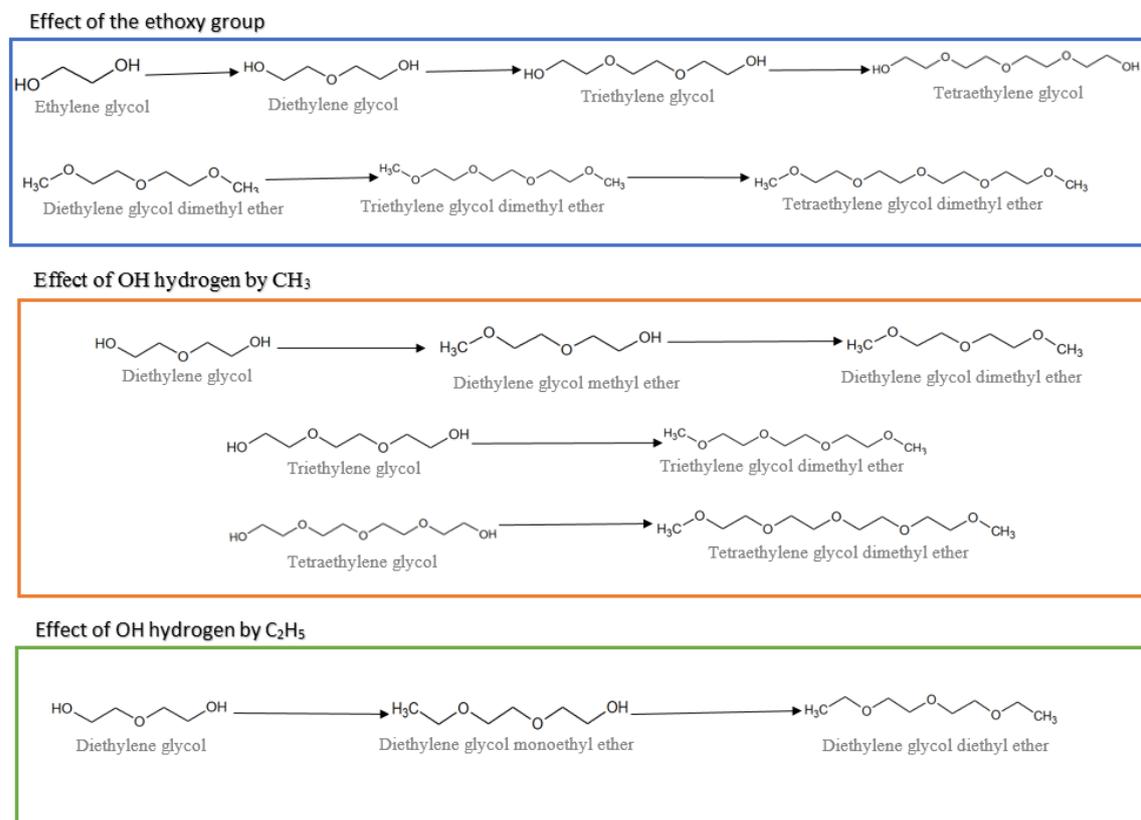
viscosity, relatively low vapour pressure and low toxicity, which make them compounds of interest in a wide set of industry applications. They have been widely used in many laboratories and commercial applications, for example as precursors in polymerization and reactions involving alkali metals, as extraction solvent for metals and organic compound, in gas purification, adsorption refrigeration, present in formulation of adhesives and coatings, in textiles, solvents for electronic industry, pharmaceutical formulation, batteries and cleaning solutions<sup>[10,11]</sup>.

Glycol ethers present also different but relevant properties which make these compounds feasible candidates for a large array of applications. Traditionally, glycol ethers are divided in two groups: e-series and p-series, depending on their ethylene or propylene precursors<sup>[12]</sup>. Generally, glycol ether are broadly used as industrial and biological solvents, surfactants, detergents, lubricants, hydraulic fluid and wetting agents<sup>[12]</sup>. In addition, they can also be used as scrubbing liquids in the cleaning of exhaust of air and gas stream in many industrial plant but also as polar additives in anionic polymerization<sup>[13]</sup>.

In spite of these compounds' inherent interest, their thermophysical properties are not extensively and accurately characterized. In fact, properties like density<sup>[14-19]</sup>, viscosity<sup>[16,20-23,23-27]</sup>, refractive index<sup>[17,22,28-31]</sup>, surface tensions<sup>[13,32-34]</sup> or heat capacities<sup>[35-40]</sup>, just to mention some, are not widely available on a wide range of temperatures and pressures. For instance, density and viscosity, provable two of the most relevant properties for process design, are reported mostly either on a narrow temperature range or at a single temperature and pressure. Thus, the accurate characterization of these compounds thermophysical properties, like density, viscosity, speed of sound and refractive index, is of key relevance if one aims at their accurate characterization, or the development/optimization of theoretical models, correlations or Equations of State (EoS)<sup>[41]</sup>. Aiming to overcome these limitation, a set of compounds were selected, namely ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (triEG), tetraethylene glycol (tetraEG), ethylene glycol monoethyl ether (EGMEE), diethylene glycol methyl ether (DEGME), diethylene glycol dimethyl ether (DEGDME), diethylene glycol monoethyl ether (DEGMEE), diethylene glycol diethyl ether (DEGDDEE), triethylene glycol dimethyl ether (triEGDME) and tetraethylene glycol dimethyl ether (tetraEGDME), in order to fully characterize their thermophysical properties on the (288.15 to 373.15) K temperature range and at atmospheric pressure. Apart from their properties characterization, the set of compounds selected allows to study the effect of the molecule chain length, and therefore the increase of the number of ether groups, and the effect of replacing the hydrogen(s) of the glycols hydroxyl group(s) by a methyl (CH<sub>3</sub>) or by an ethyl (C<sub>2</sub>H<sub>5</sub>) group on

## 1. General Introduction

the compounds properties. The knowledge of the compound's molecular structure and its properties allows one to select the best compound for a specific application and/or process. All the effect analysed in this work with the respective molecules are depicted in Figure 1.1.2.



**Figure 1.1.2-**Representation of all effects studied.

Despite the necessity for reliable experimental data, their determination can be expensive and time consuming. Thus, the development of thermodynamic models able to describe or even predict these data in a wide range of conditions is extremely relevant<sup>[42]</sup>. Even though reliable models and equations of state, able to describe these systems phase equilibrium, exists their development and optimization to describe derivative or transport properties like heat capacity, enthalpy, thermal conductivities, etc., is still of great need<sup>[43]</sup>.

Several thermodynamics models are available and able to describe the phase equilibria of these families of compounds. The best known are the NRTL<sup>[44]</sup>, UNIQUAC<sup>[45]</sup>, and the most used group contribution model in the industry, the UNIFAC model<sup>[46]</sup>, and are able to describe apolar, polar and associating systems<sup>[47]</sup>, but can be only used at low pressures (<10 bar). Moreover, they cannot deal with thermophysical properties<sup>[47]</sup>. Despite the success of these model to describe the phase equilibria, to describe the properties in a broader range of temperatures and pressures, equations of state (EoS) are more appropriate<sup>[48]</sup>.

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The SRK (Soave-Redlich-Kwong) EoS<sup>[48]</sup> and PR(Peng-Robinson)<sup>[48]</sup> are the most popular cubic equations of state, however, they are known to perform poorly for systems containing polar and hydrogen bonding molecules<sup>[47]</sup>, so, they are not appropriate for glycols. Thus, more complex thermodynamics models are required, like association equations of state, namely SAFT (statistical associating fluid theory) and CPA (Cubic Plus Association) EoS. CPA EoS, proposed by Kontogeorgs et al.<sup>[49]</sup>, combines the classical simple SRK equations with an advanced association term which is also similar to that of SAFT-type EoS. CPA EoS has been developed and evaluated for the description of the phase equilibria of mixtures containing hydrocarbon, alcohols, water, organic salts and even glycols<sup>[50]</sup>. The CPA EoS is expressed as a sum of two contributions: one accounting for the physical interaction and another accounting for association, using the Wertheim association term<sup>[50]</sup>. SAFT-type EoSs are becoming very popular in both academy and industry due to their success in predicting thermodynamic properties for a wide variety of compounds and mixtures. The SAFT-type EoS are more complex than a cubic equation of state but significantly more accurate for complex systems, such as hydrogen bonding fluids, supercritical conditions and polymers<sup>[51]</sup>. SAFT-type EoSs are available on a large diversity of versions, namely PC-SAFT<sup>[52]</sup>, VR-SAFT<sup>[53]</sup> and soft-SAFT<sup>[54]</sup>, depending on the reference fluid used. Among those, soft-SAFT EoS stands out as the most successful SAFT-type EoS.

Pedrosa et al.<sup>[8]</sup> applied the soft-SAFT EoS to describe the vapour-liquid equilibrium of glycols, namely ethylene glycol, diethylene glycol, triethylene glycol and tetraethylene glycol. Due to soft-SAFT EoS capability to model glycol systems, shown before<sup>[8]</sup>, and the possibility of extend it to other glycols places soft-SAFT EoS as the best choice to model the experimental data.

### 1.2 Scope and objectives

Despite the interest from different industrial sectors, there is still a lack of quality data of thermophysical properties for glycol and glymes in a wide range of temperatures and pressures. Thus, to overcome such demand experimental density, viscosity and refractive indices of 11 compounds were determined in the (288.15 - 373.15) K range of temperatures and at atmospheric pressure. The set of compounds, namely ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (triEG), tetraethylene glycol (tetraEG), ethylene glycol ethyl ether (EGEE), diethylene glycol methyl ether (DEGME), diethylene glycol dimethyl ether (DEGDME), diethylene glycol ethyl ether (DEGEE), diethylene glycol diethyl ether

(DEGDDEE), triethylene glycol dimethyl ether (triEGDME) and tetraethylene glycol dimethyl ether (tetraEGDME) were selected in order to fully characterize their thermophysical properties and overcome the lack of data. Furthermore, apart from their properties characterization the set of compounds here selected allows to study the effect of the molecule chain length, and therefore the increase of ether groups, the effect of replacing the hydrogen(s) of the glycols hydroxyl group(s) by a methyl ( $\text{CH}_3$ ) or by an ethyl ( $-\text{C}_2\text{H}_5$ ) group and the replacing of the ethyl ( $-\text{C}_2\text{H}_5$ ) by a methyl ( $\text{CH}_3$ ) on the compounds properties, as discussed in **Chapter 4**.

All these effects of changing the compounds structure, through the manipulation of the functional groups, stands as a relevant tool to the design of compounds and are discussed in detail in **Chapter 4**.

An analysis of the data available in the literature and those measured here allowed to evaluate the quality of the properties here determined and to identify those most reliable available in the literature. Furthermore, the soft-SAFT EoS was applied to the experimental data and new molecular parameters were proposed for the compounds under study, as discussed in **Chapter 3**. An important step on modelling is to identify which association scheme better describes the compounds. Hence, in **Chapter 3** the association model proposed for glycols by Pedrosa et al.<sup>[8]</sup> was evaluated and tested against others evaluated. Based on the association scheme selected, new optimized molecular parameters were proposed and discussed in **Chapter 3**. Furthermore, following the Pamiès et al.<sup>[55]</sup> and Pedrosa et al.<sup>[8]</sup> discussion, it was showed that the molecular parameters proposed retain their physical meaning, presenting a linear tendency with the compounds molecular weight increase. Moreover, soft-SAFT was further used to predict the properties here studied for a wider range of temperatures.

Even though the soft-SAFT EoS, with the molecular parameters proposed, provides a good description of the properties evaluated, some discrepancies and loss of accuracy is observed for the glymes with the temperature increase. With that in mind, and following the discussion reported by Kontogeorgis et al.<sup>[56]</sup>, that the molecular parameters optimized by using large sets of properties assure a better description for more complex systems, new soft-SAFT molecular parameters determined by using heat capacities together with density (liquid and vapour phase) and vapour pressures were evaluated, as discussed in **Chapter 4**. It will be shown that, overall, the use of heat capacities, to fit the compound molecular parameters, leads to a better description of the compound's properties.

Recognizing the relevance of EoSs their use can be, at times, challenging mainly for

## *1. General Introduction*

systems composed of compounds with negligible vapour pressures or with critical properties difficult to be determined. Moreover, EoSs applicability is complex and therefore, the use of empiric correlations, like those of group contribution methods, stands as a simple and easy method to determine the compounds properties for simple calculations. However, the development of group contribution methods relies on the existence of reliable experimental data. Here, taking advantage of the heat capacities gathered to enhance the soft-SAFT molecular parameters determination, a group contribution model, proposed by Růžička et al.<sup>[1,2]</sup> was evaluated at **Chapter 4**.

Finally, to sum up all the work, the conclusions and some suggestions of future work will be presented afterward.

## 2. Material and Methods



## 2.1. Compounds

Eleven glycols were studied in this work, namely ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TriEG), tetraethylene glycol (TetraEG), ethylene glycol monoethyl ether (EGMEE), diethylene glycol methyl ether (DEGME), diethylene glycol dimethyl ether (DEGDME), diethylene glycol monoethyl ether (DEGMEE), diethylene glycol diethyl ether (DEGDDE), triethylene glycol dimethyl ether (TriEGDME) and tetraethylene glycol dimethyl ether (TetraEGDME). The compounds chemical structures, purities, suppliers and corresponding designations are presented in **Table 2.1.1**.

**Table 2.1.1**- List of the compounds studied, abbreviation, purity, structure and water content.

Chemical	Abbreviation	Supplier	Purity	Structure	Water mass fraction
Diethylene glycol	DEG	SIGMA ALDRICH	≥99%		1.6x10 <sup>-3</sup>
Diethylene glycol diethyl ether	DEGDDE	ACROS ORGANIC	98+%		6.6x10 <sup>-4</sup>
Diethylene glycol dimethyl ether	DEGDME	SIGMA ALDRICH	99.50%		1.6x10 <sup>-2</sup>
Diethylene glycol methyl ether	DEGME	SIGMA ALDRICH	99%		1.5x10 <sup>-3</sup>
Diethylene glycol monoethyl ether	DEGMEE	ACROS ORGANIC	98+%		2.9x10 <sup>-4</sup>
Ethylene glycol	EG	FLUKA	99.5%		7.9x10 <sup>-4</sup>
Ethylene glycol monoethyl ether	EGMEE	PANREAC	99%		4.1x10 <sup>-3</sup>
Tetraethylene glycol	TetraEG	SIGMA ALDRICH	99%		1.9x10 <sup>-3</sup>
Tetraethylene glycol dimethyl ether	TetraEGDME	SIGMA ALDRICH	≥99%		1.7x10 <sup>-4</sup>
Triethylene glycol	TriEG	SIGMA ALDRICH	≥99%		1.2x10 <sup>-3</sup>
Triethylene glycol dimethyl ether	TriEGDME	SIGMA ALDRICH	99%		1.5x10 <sup>-4</sup>

## 2.2. Purification Procedure

It is well established that even small amounts of water and other impurities have a great impact on the compound's thermophysical properties, especially on properties like viscosity, interfacial tension or refractive index. Thus, in order to reduce to negligible values both water and volatile solvents, individual samples of each glycol and glyme were dried under vacuum (0.1 Pa), moderate temperature (303.15 K) and under constant stirring for a period of at least 48 h prior to the measurements. For this purpose a vacuum line, depicted in Figure 2.2.1a), was used. The final water content, after the drying process and immediately before the measurements, was determined with a Metrohm 831 Karl-Fisher coulometer (Figure 2.2.1b) using the Hydranal - Coulomat AG from Riedel-de Haën as analyte. The purification procedure

## 2. Material and Equipment

adopted assured very low water contents with the average water contents <100ppm, as presented in **Table 2.1.1**.

Even though most of the glycols studied present negligible vapour pressures under the drying conditions adopted and therefore, the procedure above mentioned can be applied without loss of the glycol, the diethylene glycol dimethyl ether (DEGDME) and ethylene glycol monoethyl ether (EGMEE) have higher vapour pressures and thus can be distilled. Therefore, for these compounds the purification procedure was modified and in order to reduce their water and volatile compounds content, a two-steps distillation was adopted. During the distillation an initial amount of distillate (5 mL) was discarded while the remaining compound was further distilled and the distillate used. This procedure was applied immediately before the property determination and repeated between measurements to remove traces of water absorbed during the compound manipulation.



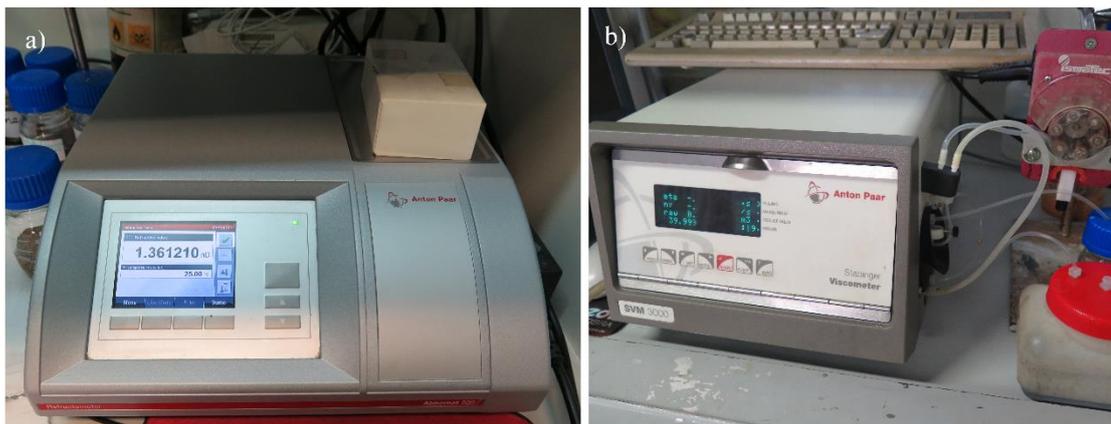
**Figure 2.2.1-** Vacuum line for the drying process (a) and Metrohm 831 Karl-Fisher Coulometer (b).

### 2.3. Equipment and methodology

Measurements of viscosity ( $\rho$ ) and density ( $\eta$ ) were carried out in the (288.15 - 373.15) K temperature range and at atmospheric pressure using an Anton Paar SVM 3000 automated rotational Stabinger viscosimeter-densimeter (Figure 2.2.1b) within an absolute uncertainty of  $\pm 5 \times 10^{-4} \text{ g cm}^{-3}$  on the density and  $\pm 1\%$  relative uncertainty on the dynamic viscosity. The relative uncertainty on the temperature is within  $\pm 0.02 \text{ }^\circ\text{C}$ . Further details regarding the use of the equipment and methodologies for the determination of densities and viscosities can be

found elsewhere<sup>[57]</sup>.

It is worth noting that several compounds present very low viscosities and therefore an ultra-low viscosity calibration was required to assure accurate data determination. Thus, in order to experimentally determine these viscosities, the SVM3000 viscometer-densimeter was calibrated for ultra-low viscosity by using *n*-octane as the reference fluid. Within this ultra-low viscosity calibration (0.360 to 1.271 mPa.s) the dynamic viscosity relative uncertainty is  $\pm 2.8\%$ .



**Figure 2.3.1-** Abbemat 500 Paar refractometer (a) and Stabinger SVM 3000 viscosimeter-densimeter (b).

Measurements of refractive indices ( $n_D$ ) were performed in the 589.3 nm wave length using an automated *Abbemat 500 Anton Paar* refractometer. Refractive index measurements were carried out in the (283.15 - 353.15) K temperature range and at atmospheric pressure. The Anton Paar Abbemat 500 uses reflected light to measure the refractive index, where the sample added on the top of the measuring prism is irradiated from different angles by a light emitting diode (LED). The maximum deviation in the temperature is  $\pm 0.05^\circ\text{C}$ , and the maximum uncertainty in the refractive index is  $\pm 2 \times 10^{-5} n_D$ . The measurement of the refractive index, with the equipment used, is simple and straightforward. However, some concerns must be addressed. As known the studied compounds are hygroscopic and therefore precautions to avoid moisture absorption during manipulation and the measurements must be taken. To overcome water absorption during the measurements on top of the equipment tap a dry chamber was created by placing silica gel inside an aluminum box that covered the entire measurement cell. In fact, without this methodology instability of the measurements was observed for temperatures above  $60^\circ\text{C}$ .



## 3. Modelling



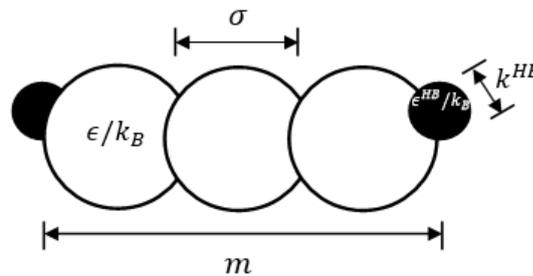
### 3.1. Soft-SAFT EoS

The soft-SAFT, a version of SAFT-type equations of state, proposed by Vega and co-workers<sup>[55,58,59]</sup> is the most successful of their type. This equation is able to successfully describe the phase behaviour, as well as, thermophysical properties both of non-self-associating compounds, such as of *n*-alkanes<sup>[55]</sup> and perfluorocarbons<sup>[60]</sup>, and associating compounds, like alcohols and their mixtures<sup>[61]</sup>. Moreover, Pedrosa and co-workers<sup>[8]</sup>, successfully extended the soft-SAFT for glycols, namely EG, DEG, TriEG and TetraEG.

The general expression for SAFT is given in terms of the residual Helmholtz energy,  $A^{res}$ , defined as the molar Helmholtz energy of the fluid relative to that of an ideal gas at the same temperature, density and composition. This residual Helmholtz energy can be express as the sum of different microscopic contributions with the general expression of the SAFT equation being described as:

$$A^{res} = A^{total} - A^{ideal} = A^{ref} + A^{chain} + A^{assoc} + A^{polar} \quad \text{Eq. 3.1}$$

where the superscripts *ref*, *chain*, *assoc* and *ideal* refer to a contribution from the reference term, the formation of the chain, the association and polar interaction, respectively. A hypothetical model of an association molecule modelled by the soft-SAFT approach is depicted in Figure 3.1.1, where the segment number ( $m$ ), the segment size ( $\sigma$ ), the dispersive energy between segment ( $\epsilon/k_B$ ), the energy ( $\epsilon^{HB}/k_B$ ) and volume ( $k^{HB}$ ) of association per site are molecular parameters needed by the EoS to model compounds.



**Figure 3.1.1-** Molecular model proposed within the soft-SAFT<sup>[8]</sup>.

The Helmholtz energy for a pure ideal fluid,  $A^{ideal}$ , is given by:

$$A^{ideal} = RT (\ln \rho - 1) \quad \text{Eq. 3.2}$$

The reference term,  $A^{ref}$ , usually describes the properties of the individual units that compose the chain. Each version of SAFT EoSs use different terms for the reference fluid; while the original SAFT<sup>[62]</sup> uses a reference fluid based on hard-spheres, with a perturbative term to take into account the dispersive forces, the SAFT-VR<sup>[53]</sup> applies a square-well-potential of variable range. A perturbed hard-chain<sup>[52]</sup> is used in the case of PC-SAFT, and

### 3. Modelling

finally soft-SAFT<sup>[63,64]</sup> uses a Lennard Jones (LJ) spherical fluid, a “soft” reference fluid, which takes into account the repulsive and attractive interactions of the segments forming the chain modelled by the Lennard-Jones EoS. This equation was obtained by fitting simulation data to the modified Benedict-Webb-Rubins EoS in which molecular parameters for other compounds can be extended to mixtures by applying the van der Waals one-fluid theory (vdW-1f)<sup>[65]</sup>.

The chain,  $A^{chain}$ , and association,  $A^{assoc}$ , term are normally identical for all SAFT-types and are derived from the Wertheim’s theory (TPT1):

$$A^{chain} = \rho k_B T \sum_i x_i (1 - m_i) \ln g_{LJ} \quad \text{Eq. 3.3}$$

$$A^{assoc} = \rho k_B T \sum_i x_i \left( \sum_{\alpha} X_i^{\alpha} - X_i^{\alpha} + \frac{M_i}{2} \right) \quad \text{Eq. 3.4}$$

where  $\rho$  is the molar density,  $k_B$  is the Boltzmann’s constant,  $T$  is the temperature,  $x_i$  is the molar fraction of component  $i$ ,  $m$  the chain length,  $g_{LJ}$  is the radial distribution function of a fluid of LJ spheres at density  $\rho_m = m \rho$  and evaluated at the bond length  $\sigma$ ,  $M_i$  is the number of association sites in component  $i$  and  $X_i^{\alpha}$  is the mole fraction of molecules of components  $i$  nonbonded at site  $\alpha$ , which extends over all  $i$  compounds in the mixture.

Finally,  $A^{polar}$ , the main polar interaction can be taken into account in the model by adding new parameter, the quadrupole moment  $Q$ . The calculation of this parameter is for linear symmetrical molecules, like carbon dioxide, nitrogen, or aromatic compounds.

In order to apply the soft-SAFT EoS for a particular system it is imperative to specify the molecular model of each compound (number of association sites for each molecule and allowed interactions among the sites) as well as to obtain its molecular parameters. The molecular parameter are commonly fitted against experimental vapour pressure and saturated liquid density data over a determined range of temperatures using the following objective functions<sup>[64]</sup>:

$$f_1(m, \sigma, \varepsilon/k_B, \varepsilon^{HB}/k_B, k_{HB}) = \sum_i^N [\rho_i^{exp} - \rho_i^{calc}(p_i^{exp}, T_i^{exp})]^2 \quad \text{Eq. 3.5}$$

$$f_2(m, \sigma, \varepsilon/k_B, \varepsilon^{HB}/k_B, k_{HB}) = \sum_i^N [\mu_{i,liq}^{calc}(p_i^{exp}, T_i^{exp}) - \mu_{i,vap}^{calc}(p_i^{exp}, T_i^{exp})]^2 \quad \text{Eq. 3.6}$$

where  $N$  is the number of experimental points,  $p_i^{exp}$ ,  $T_i^{exp}$  and  $\rho_i^{exp}$  are the vapour pressure, the temperature and the liquid molar density corresponding to the experimental point  $i$ ,

respectively. The variables  $\rho_i^{calc}$ ,  $\mu_{i,liq}^{calc}$  and  $\mu_{i,vap}^{calc}$  refer to the saturated liquid density and the chemical potentials of the liquid and the vapour phase, respectively, calculated by the soft-SAFT at temperature  $T_i^{exp}$  and pressure  $p_i^{exp}$ . The two functions  $f$  are minimized using the Marquart-Levenberg algorithm<sup>[66]</sup> and the process stopped when  $f_1 - f_2 \leq 10^{-6}$ .

Once the residual Helmholtz energy is obtained the chemical potential and the pressure can also be calculated through the first derivative of the functions<sup>[67]</sup>:

$$p = - \left( \frac{\partial A}{\partial V} \right)_{T,w} \quad \text{Eq. 3.7}$$

$$\mu_i = \left( \frac{\partial A}{\partial n_i} \right)_{n_j, T, P} \quad \text{Eq. 3.8}$$

In the same manner, second order derivative properties calculated in this work, are implemented into the code by applying the following equations<sup>[67,68]</sup>

$$C_v = -T \left( \frac{\partial^2 A}{\partial T^2} \right)_v \quad \text{Eq. 3.9}$$

$$k_T^{-1} = \rho \left( \frac{\partial P}{\partial \rho} \right)_T \quad \text{Eq. 3.10}$$

$$\mu_{JT} = T \left( \frac{\partial P}{\partial T} \right)_v - \rho \left( \frac{\partial P}{\partial \rho} \right)_T \quad \text{Eq. 3.11}$$

$$\alpha_p = k_T \left( \frac{\partial P}{\partial T} \right)_v \quad \text{Eq. 3.12}$$

$$C_p = C_v + \frac{(T \alpha_p^2)}{k_T \rho} \quad \text{Eq. 3.13}$$

$$k_s = k_T \left( \frac{C_v}{C_p} \right) \quad \text{Eq.3.14}$$

$$u = \sqrt{\frac{C_p}{C_v} \left( \frac{\partial P}{\partial \rho} \right)_T} \quad \text{Eq.3.15}$$

where  $C_v$  is the residual isochoric heat capacity,  $k_T$  the isothermal compressibility coefficient,  $C_p$  the isobaric residual heat capacity,  $\mu_{JT}$  is the Joule-Thomson coefficient,  $\alpha_p$  the thermal expansion coefficient,  $k_s$  the isentropic compressibility coefficient and  $u$  is the speed of sound. Since soft-SAFT allows to determine only the residual heat capacity, the ideal heat capacity is required in order to determine the compounds' isobaric heat capacity.

Recently Llovell and co-workers<sup>[69]</sup> introduced into the soft-SAFT package the possibility to determine viscosities. In a recent paper the authors reported the use of soft-SAFT for the

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viscosity determination of water and 1-alkanols using a Free-Energy approach<sup>[70]</sup>. The soft-SAFT EoS viscosity determination is carried out by coupling the Free-Volume Theory (FVT) approach, proposed by Allal et al.<sup>[71]</sup>, to the EoS. The FVT treatment proposes a division of the dynamic viscosity into the viscosity of dilute gas,  $\eta_0$ , and a dense-state correction term  $\Delta\eta_c$ .

$$\eta = \eta_0 + \Delta\eta_c \quad \text{Eq. 3.16}$$

where,  $\eta_0$  is obtained by the expression reported by Chueng et al.<sup>[72]</sup>. The dense-state correction term,  $\Delta\eta$ , is related to the molecular structure through an empirical relation of the free-volume fractions,  $f_v$ , proposed by Doolittle et al.<sup>[73]</sup> based on Allal et al.<sup>[71]</sup> work, where they related the free-volume fractions with the intermolecular energy controlling the potential field in which the molecular diffusion takes place.

$$\Delta\eta_c = A \exp\left(\frac{B}{f_v}\right) \quad \text{Eq. 3.17}$$

The expression for viscosity (viscosity in Pa. s) can be rewritten as:

$$\Delta\eta_c = L_v(0.1p + 10^{-4}\alpha\rho^2M_w) \sqrt{\frac{10^{-3}M_w}{3RT}} \exp\left[B\left(\frac{10^3p + \alpha}{\rho RT}\right)^{3/2}\right] \quad \text{Eq. 3.18}$$

where  $R$  is the universal constant in J/(mol K),  $M_w$  is the molecular weight in g/mol,  $T$  is the temperature in K,  $\rho$  the molar density in mol/L and  $p$  the pressure in MPa. The equation 3.17 includes three new adjustable parameters,  $\alpha$  (J m<sup>3</sup>/(mol kg)) which describes the proportionality between the energy barrier and the density,  $B$  that corresponds to the free volume overlap and  $L_v$  (Å) that is the length parameter related to the structure of the molecules and the characteristic relaxation time. The compounds properties like  $T_c$ ,  $p_c$  and  $\omega$  were taken from DIPPR<sup>[74]</sup>. These new adjustable parameters are determined by fitting the EoS against experimental viscosity data.

#### 3.1.1. Molecular parameters

The soft-SAFT molecular parameters for a wide set of compound families, like alkanes<sup>[58,64,68]</sup>, polymers<sup>[8,75]</sup>, perfluoralkanes<sup>[76]</sup> and more recently to ionic liquids<sup>[77,78]</sup>, are widely available in the literature. Only Pedrosa et al.<sup>[8]</sup> proposed molecular parameters for the description of ethylene glycol and its oligomers using the soft-SAFT EoS.

As mentioned above, in order to determine the compound's molecular parameters it is necessary to identify the association scheme that better describes the compound properties. The association scheme proposed by Pedrosa et al.<sup>[8]</sup>, for glycols, identifies only AA interactions,

with site “A” representing the specific associations due to the hydroxyl group ( $-OH$ ) at the terminals of the molecule chain (see Table 3.1.1). Moreover, it is worth mentioning that some authors<sup>[79]</sup> including Pedrosa et al.<sup>[8]</sup>, state that ether groups ( $-O-$ ) on the glycols, present no association.

**Table 3.1.1** Association schemes proposed for the compounds studied.

Model	Number of sites	Association schemes	Allowed association
N	0		No association No cross-association
A1	1		AA self-association
	2		AA self-association

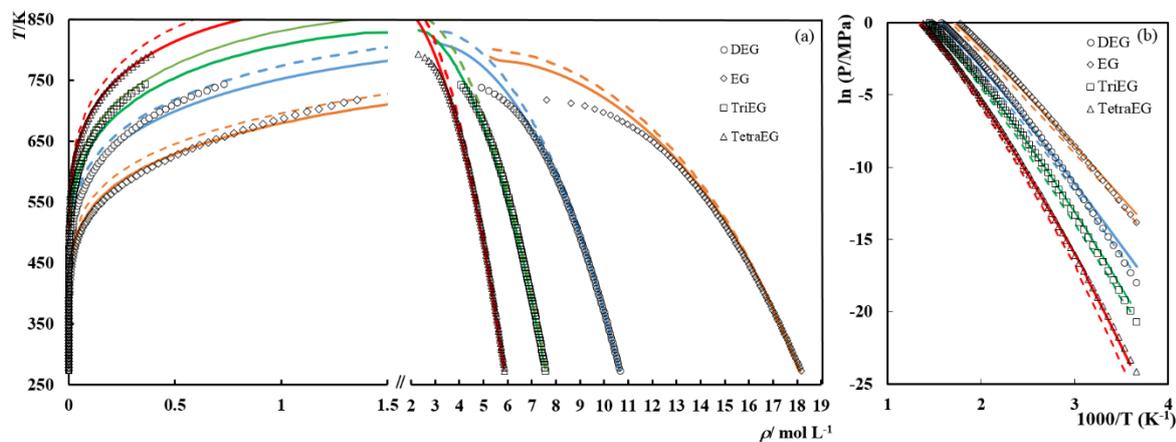
Pedrosa and co-workers<sup>[8]</sup> suggest also that the  $\epsilon^{HB}/k_B$  and  $k^{HB}$  molecular parameters should remain fixed for all the compounds of the family and equal to the ones of ethylene glycol. Nevertheless, no reasoning was given for justifying that assumption: no test for the parameters values dependency with the compound chain length or molecular weight was carried out and presented, and no quantum-mechanical calculations were used to investigate the proper association-energy parameter values of the associative molecules through liquid-phase hydrogen-bonding enthalpy information. Moreover, most probably due to the updates done to the soft-SAFT code over the years the results given by our version of the soft-SAFT code, using the molecular parameter proposed by Pedrosa et al.<sup>[8]</sup>, did not provide the same results as those reported by the authors. In fact, the most recent soft-SAFT version provide worse results than those presented by Pedrosa et al.<sup>[8]</sup>. Thus, since we do not find justifiable the above described approach nor can we be assured that the molecular parameters proposed by the authors are in fact representative of the functional group association volume and energy, new molecular parameters were determined and evaluated for the compounds families here studied.

The molecular parameters were then fitted against the density data here measured, and vapour pressures taken from literature<sup>[74]</sup>. It is worth mention that, despite the range of data available, the data used respected the EoS limitation of  $0.45 < T_r < 0.90$ .

In order to see the ability of our molecular parameters in describing the liquid and the vapour phase density for temperatures near the critical region, soft-SAFT was used in a predictive manner to describe the density of glycols. As depicted in Figure 3.1.2, it can be observed that the new molecular parameters present a better description of the density, as well as the vapour pressure, than those proposed by using the molecular parameters from Pedrosa et

### 3. Modelling

al.<sup>[8]</sup>. Within the same temperature range smaller percentage absolute average deviations (1.4% for the density and 19.3% for vapour pressures) were obtained with the new set of molecular parameters, in comparison with those obtained by the authors<sup>[8]</sup> (2.5% for density and 38.9% for vapour pressure). %AAD for each compound are reported in Table 3.1.5.



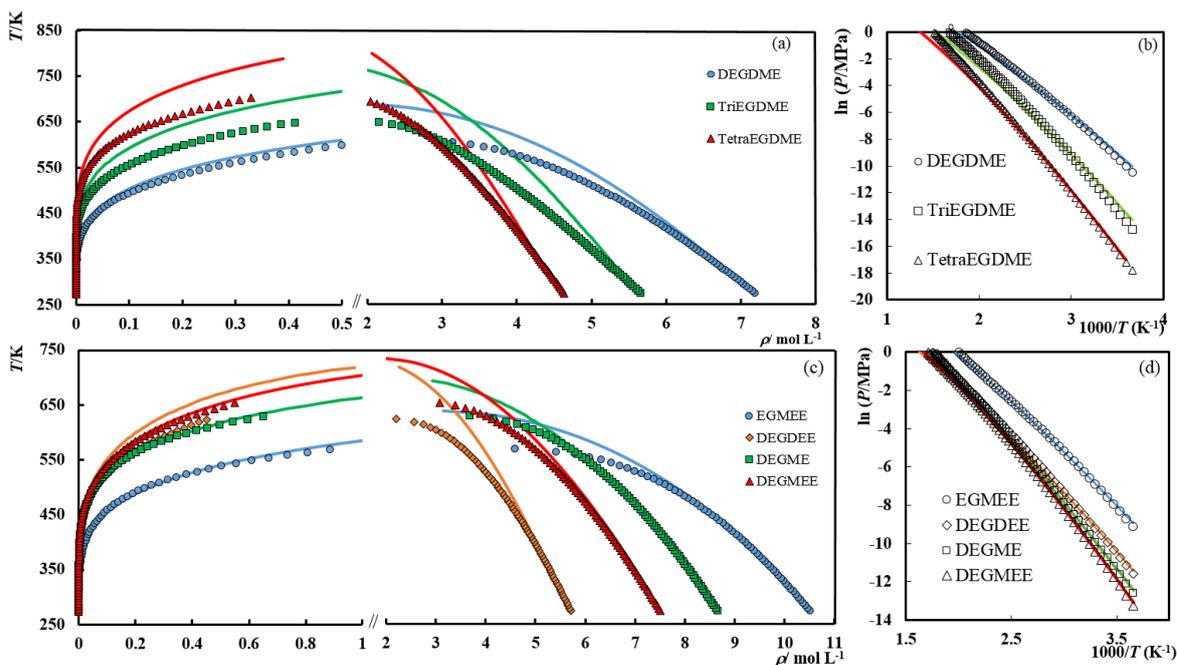
**Figure 3.1.2-** Density of the vapour and liquid phases as function of temperature (a) and the logarithm of vapour pressure as function of the temperature (b) for ethylene glycol, di, tri and tetraethylene glycol. Symbols represents the experimental data taken from DIPPR<sup>[74]</sup> and the solid and dashed lines corresponds to the soft-SAFT results using ours and Pedrosa et al.<sup>[8]</sup> molecular parameters, respectively.

Since the molecular scheme adopted allows soft-SAFT to describe correctly the glycols (diols), new molecular parameters for the remaining compounds here studied were determined according to the associative scheme reported in the Table 3.1.1. Similar to the case of the diols, new molecular parameters proposed, and reported in Table 3.1.2, allow soft-SAFT to describe not only the density within the temperature range used for the fitting, with %AAD ranging from 0.028% to 0.62% for density and 2.0% to 8.8% for vapour pressure, but also the entire phase diagram. Naturally the critical region is over estimated but that is a well-known limitation of the EoSs and therefore an expected behaviour.

**Table 3.1.2-** soft-SAFT molecular parameters, temperature range of the experimental data used for the parameters fit and %AAD between the experimental and calculated density and vapour pressure data, for the studied compounds.

Compound	T/K		Molecular parameters					%AAD	
	Tmin	Tmax	m	$\sigma$ (Å)	$\varepsilon/k_B$ (K)	$\varepsilon^{HB}/k_B$ (K)	$k^{HB}$ (Å)	$\rho$	$p$
Ethylene glycol	328.15	373.15	1.848	3.596	325.05	4103.0	4336.5	0.061	5.841
Diethylene glycol	338.15	373.15	2.549	3.851	324.28	4353.2	3800.0	0.028	7.198
Triethylene glycol	348.15	373.15	3.189	4.010	333.09	4238.5	4075.1	0.031	3.802
Tetraethylene glycol	348.15	373.15	4.041	4.033	330.49	4374.0	4075.0	0.226	2.029
Diethylene glycol dimethyl ether	328.15	373.15	3.377	3.912	304.75			0.072	3.769
Diethylene glycol diethyl ether	288.15	373.15	3.126	4.376	335.50			0.263	6.860
Triethylene glycol dimethyl ether	328.15	373.15	3.853	4.099	328.36			0.057	8.757
Tetraethylene glycol dimethyl ether	318.15	373.15	4.158	4.306	352.02			0.615	5.922
Ethylene glycol monoethyl ether	288.15	373.15	2.318	3.922	295.83	3904.4	4393.2	0.048	3.740
Diethylene glycol methyl ether	288.15	373.15	2.990	3.836	283.81	4835.1	5053.7	0.232	4.207
Diethylene glycol monoethyl ether	288.15	373.15	3.416	3.888	318.68	3152.9	3599.1	0.075	3.107

The description of soft-SAFT, using the proposed molecular parameters and association scheme, for vapour and liquid phase densities as well as for the vapour pressures are depicted in Figure 3.1.3.



**Figure 3.1.3-** Density of the vapour and liquid phases as function of temperature (a and c) and the logarithm of vapour pressure as function of temperature for: diethylene glycol, tri and tetraethylene glycol (b and d); for ethylene glycol monoethyl ether and diethylene glycol diethyl ether, methyl ether and monoethyl ether (c and d). Symbols represents the experimental data taken from DIPPR<sup>[74]</sup> and the solid lines corresponds to the soft-SAFT results using the parameters proposed in this work.

As depicted in Figure 3.1.2 and Figure 3.1.3, the prediction of soft-SAFT is in very good agreement, except for the region close to the critical point. This was expected, since it was used an analytical equation of state, in which the density fluctuation occurring at the critical region

### 3. Modelling

is not explicitly taken into account.

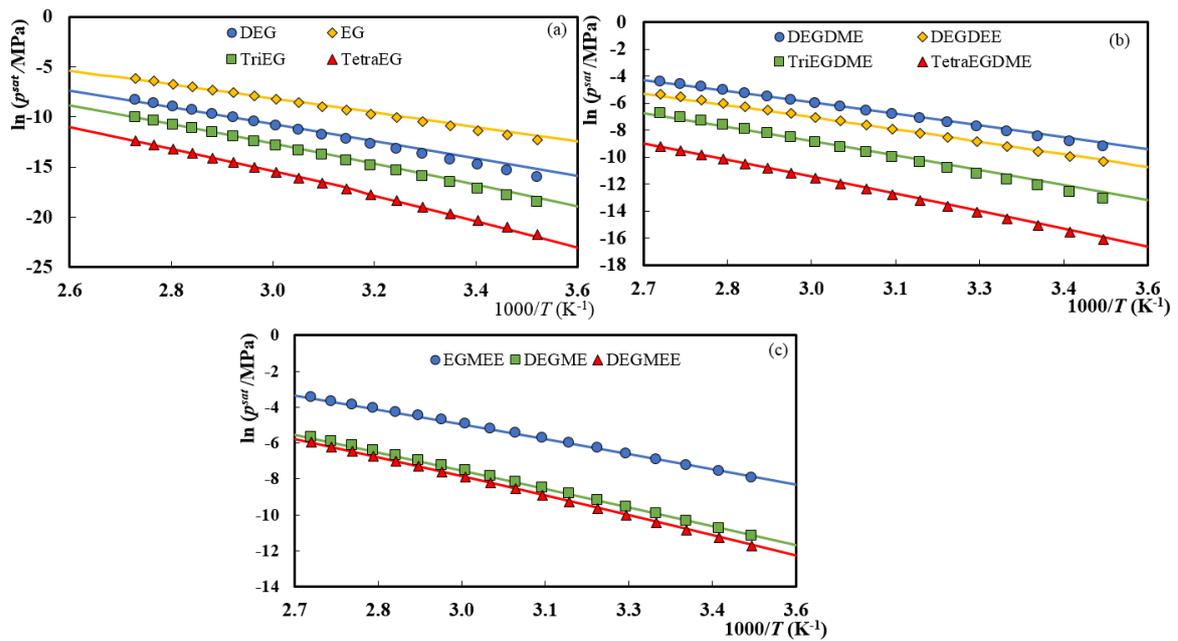
Generally, it can be stated that the density for both phases of glycols (EG, DEG, TriEG and TetraEG) are well described by soft-SAFT as for the glycols with only one hydroxyl group (EGMEE, DEGMEE and DEGME), especially for temperatures up to 550 K. In the other hand, for glymes, as depicted in Figure 3.1.3, soft-SAFT is able to describe correctly the glymes liquid density for temperatures up to 400 K and the compounds' vapour pressure on the entire temperature range evaluated. For temperatures below 400 K %AAD of 0.60%, 1.4%, 0.53% and 0.29% for the density of DEGDME, TriEGDME, TetraEGDME and DEGMEE, respectively, are obtained. Above this temperature soft-SAFT starts to overestimate the density and the deviations are reported in Table 3.1.3.

For the vapour pressure, as plotted in Figure 3.1.3 b and d, the results of soft-SAFT are in good agreement with experimental data for most of the compounds studied, but, there are still some problems in describing the vapour pressure of glymes for the higher temperatures, for which soft-SAFT underestimates this property.

**Table 3.1.3-** soft-SAFT EoS prediction modelling results for liquid and vapour phase density and vapour pressure in the (273.15 to  $T_c$ ) temperature range and at equilibrium condition.

Compound	EG	DEG	TriEG	TetraEG	DEGDME	DEGDME	TriEGDME	TetraEGDME	EGMEE	DEGMEE	DEGME
<b>Density liquid phase</b>											
$\Delta\rho_{\max}$ (mol L <sup>-1</sup> )	2.50	1.40	0.18	0.68	1.06	1.31	1.26	1.00	1.86	1.09	1.14
%AAD	1.94	1.36	0.74	1.60	4.94	5.97	11.06	8.01	2.44	3.30	1.81
<b>Density vapour phase</b>											
$\Delta\rho_{\max}$ (mol L <sup>-1</sup> )	0.29	0.15	0.07	0.00	0.08	0.18	0.20	0.18	0.12	0.04	0.06
%AAD	16.51	25.59	19.09	7.55	14.81	24.36	39.01	31.27	4.72	3.91	4.03
<b>Vapour Pressure</b>											
$\Delta p_{\max}$ (MPa)	0.06	0.02	0.00	0.00	0.11	0.09	0.06	0.01	0.12	0.01	0.02
%AAD	25.14	23.94	14.34	11.05	20.14	27.69	41.16	28.88	9.72	9.68	10.67

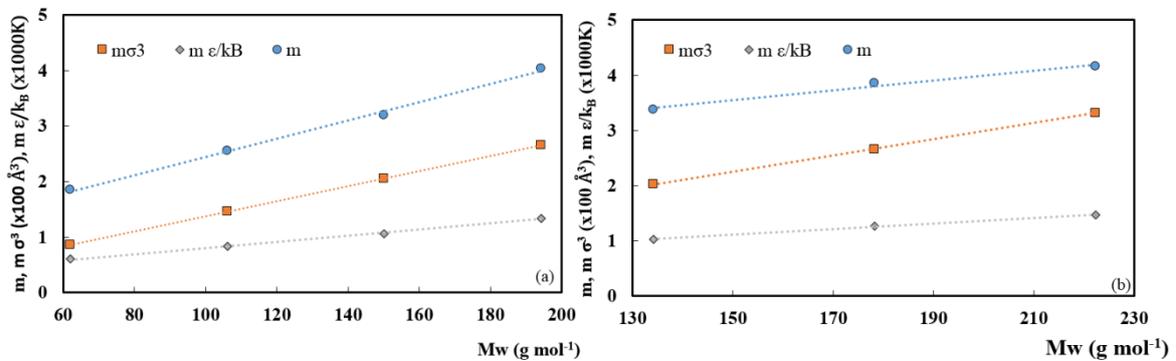
The Table 3.1.3 reports the %AAD and the maximum density differences  $\Delta\rho_{\max}$  obtained between soft-SAFT results and the experimental data for each compound, where the bigger %AAD in the density liquid phase obtained are 1.9% for ethylene glycol, 11.1% for triethylene glycol dimethyl ether and 3.3% for diethylene glycol monoethyl ether. As already shown in Figure 3.1.2b, Figure 3.1.3b and d, soft-SAFT results for the vapour pressure are in good agreement with those calculated using the correlation provided by DIPPR<sup>[74]</sup>. Bigger deviations are found, nonetheless, for ethylene glycol, triethylene glycol dimethyl ether and ethylene glycol monoethyl ether.



**Figure 3.1.4-** Representation of the  $\ln(p^{\text{sat}})$  as a function of the inverse of temperature.

Looking now, for the vapour pressure in the (288.18 - 373.15) K temperature range, depicted in Figure 3.1.4, the results show very good agreement between the soft-SAFT EoS and the experimental data, as expected, with maximum vapour pressure differences around  $1.04 \times 10^{-3}$  MPa.

In an earlier work, for the *n*-alkanes and perfluoroalkanes, Pàmies et al.<sup>[55]</sup> have shown that the soft-SAFT molecular parameters can be correlated with the molecular weight ( $M_w$ ) of the compounds, providing a physical meaning for the parameters. Later, Pedrosa et al.<sup>[8]</sup>, following this suggestion have shown that molecular parameters for glycols present the same behaviour. Here, the same approach was used in order to evaluate the consistency of the molecular parameters proposed here, and as depicted in Figure 3.1.5 a dependency of the soft-SAFT molecular parameters with the compounds' chain size increase can be also observed.



**Figure 3.1.5-** soft-SAFT  $m$ ,  $\sigma$  and  $\epsilon/k_B$  molecular parameter as function of: a) mono, di, tri and tetraethylene glycol and b) di, tri and tetraethylene glycol dimethyl ether molecular weight.

### 3. Modelling

The correlations for glycols using our molecular parameters are expressed in the following set of equations:

$$m = 0.01639 M_w + 0.8068 \quad \text{Eq. 3.19}$$

$$m \sigma^3 = 1.3563 M_w + 1.7522 \quad \text{Eq. 3.20}$$

$$m \epsilon/k_B = 5.539 M_w + 24.643 \quad \text{Eq. 3.21}$$

The correlations for glymes using our molecular parameters are expressed in the following set of equations:

$$m = 0.08862 M_w + 2.2166 \quad \text{Eq. 3.22}$$

$$m \sigma^3 = 1.4714 M_w + 4.2621 \quad \text{Eq. 3.23}$$

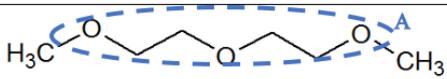
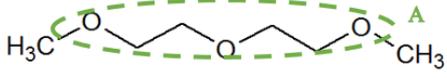
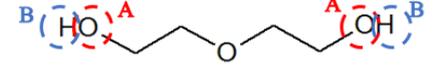
$$m \epsilon/k_B = 4.931 M_w + 373.396 \quad \text{Eq. 3.24}$$

As stated by Pamiès et al.<sup>[55]</sup>, an advantage of having parameters with physical meaning is that their physical trend can be evaluated, apart from their use in the correlation. It's important to note that when the linear correlation with the molecular weight is established, the fluctuation of the parameters may be hidden behind the multiplication by  $m$  and also by having  $\sigma^3$  instead of  $\sigma$ .

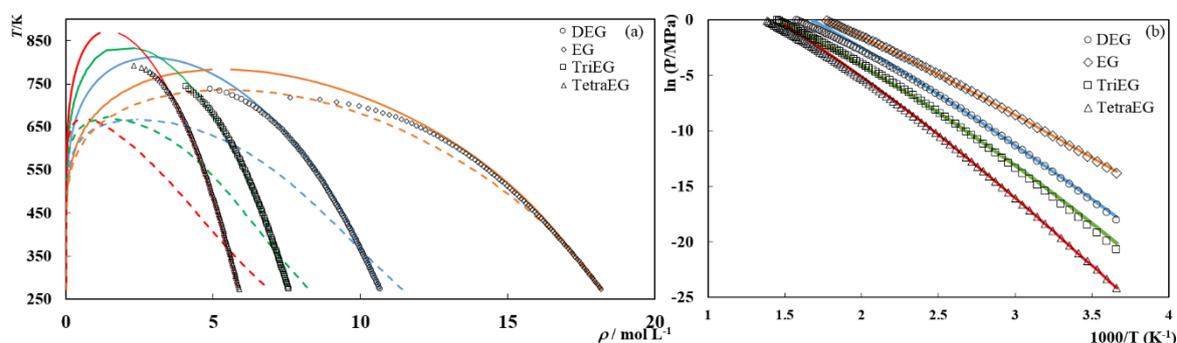
For the association molecular parameters  $\epsilon^{HB}/k_B$  and  $k^{HB}$ , it was not found the same linear tendency with the molecular weight, as it can be understood with the values reported in appendix (Figure C.2). It can be observed that when increasing the chain's length of glycols no linear tendency was observed using the soft-SAFT EoS. However for other EoS, for example with CPA-EoS, Oliveira et al.<sup>[80]</sup> observed that the association volume decreases and the energy of the interaction converge to a constant value when increasing the length of  $n$ -alcohols.

Due to this loss of accuracy with the temperature increase, namely for glymes, new association schemes were evaluated. Thus, other association schemes were investigated, one with four associating sites (model AB) for the glycols (in which association is only established between A and B sites where A and B stand for oxygen and the hydrogen on the hydroxyl group, respectively) and other with one association site for the ether groups of the molecule, in which the site A represent one of the oxygens in the molecule chain, this model is denoted as model H, and considers no self-association but only cross-association. The model A2 reported in Table 3.1.4 is equal to the model A1 in Table 3.1.3, but it was here tested for diethylene glycol dimethyl ether, where the association site A can be one of the oxygens in the ether group and this model allows self-association.

**Table 3.1.4-**Alternative association schemes tested.

Model	Number of sites	Association schemes	Allowed association
H	1		no self-association with cross-association
A2	1		AA self-association
AB	4		AB self-association

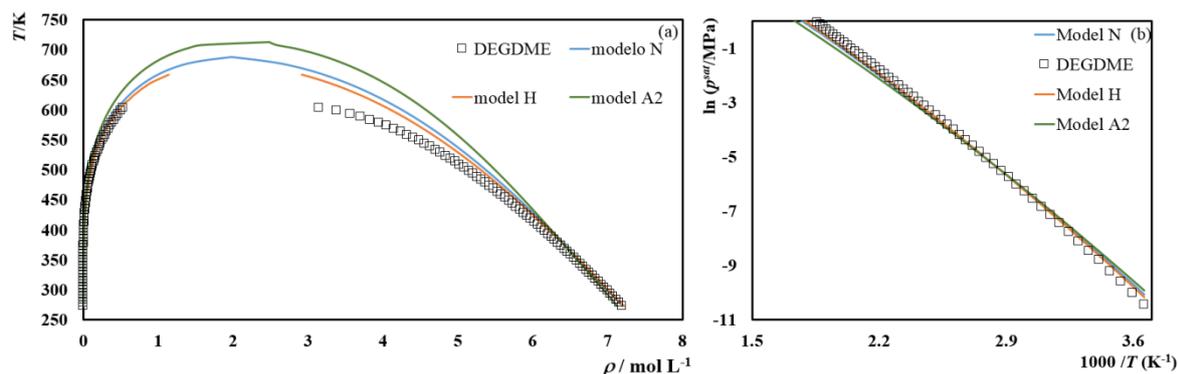
Naturally, new molecular parameters were optimized by fitting the EoS against density and vapour pressure data for each association scheme. From Figure 3.1.6 it can be seen through the results obtained with the associative model AB that it limits the soft-SAFT ability to describe the density of the liquid phase data better than the previous association scheme tested, namely for DEG, triEG and tetraEG. Despite of obtaining a very good description of the vapour pressure (see Figure 3.1.6b) the description of the compounds' densities is lost, with %AAD for, di-, tri- and tetraethylene glycol of 6.3%, 8.3% and 14.9%, respectively within the (273 - 550) K range of temperature. For ethylene glycol, the EoS description of the density is also affected but a small %AAD of 0.93% are obtained. Nonetheless, for higher temperatures higher deviations are observed and the %AADs for the entire range are reported in Table 3.1.5.



**Figure 3.1.6-** Density of the vapour and liquid phase as function of temperature for ethylene glycol and oligomers. The solid and the dashed lines correspond to the soft-SAFT results with the associative model A1 and model AB, respectively.

Looking now at the Figure 3.1.7 it is observed that the model A2 overestimates the density of diethylene glycol dimethyl ether for both phases, but on the other hand for model H, it can be observed a slightly better description of the density on the liquid phase than obtained with the model N. In fact the %AAD for the density in the range of temperature (273.15 to  $T_c$ ) K is 3.9%, 4.9% and 7.0% for model H, model N and model A2, respectively. Regarding to the vapour pressure, in Figure 3.1.7 b, the model H still presents lower deviations (15.56%) than the other two (the %ADD is 20.1% for model N and 29.6% for model A2).

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**Figure 3.1.7-** Density of the vapour and liquid phase as function of temperature for diethylene glycol dimethyl ether. The solid lines correspond to the soft-SAFT results with the three different association models.

Briefly, in spite of model H producing better results, it was not used in the rest in of this work. This decision can be justified by the similarity between the deviation values obtained for models H and N, that suggest that the lower deviation obtained with model H resulted only from a lower minimum found by the optimization routine and not from a better representation of the compound, since the same inadequacy in describing the liquid density temperature dependency at high temperatures is found for both models. Besides of that mathematical issue, the association model cannot be truly used for designing the molecule in pure state, since this model needs to be tested against phase equilibria description of mixtures in which can be taken into account the possible cross-association by hydrogen bond interaction (e.g, with water).

**Table 3.1.5-** Density and vapour pressure %AAD for the different molecular schemes tested.

% AAD	T /K		A1 (this work)		A1 (Pedrosa et al.)		N		AB		A2		H	
	$T_{min}$	$T_{max}$	$\rho$	$p^{sat}$	$\rho$	$p^{sat}$	$\rho$	$p^{sat}$	$\rho$	$p^{sat}$	$\rho$	$p^{sat}$	$\rho$	$p^{sat}$
EG	273	720	1.94	23.57	2.95	40.59			2.80	4.29				
DEG	273	745	1.36	27.59	2.87	37.28			13.82	38.46				
TriEG	273	770	0.75	14.34	1.29	36.54			17.54	49.19				
TetraEG	273	795	1.60	11.72	2.77	41.16			26.30	25.49				
DEGDME	273	608					4.94	20.14			7.016	29.36	3.854	15.56
DEGDDE	273	624					5.97	27.69						
TriEGDME	273	651					11.06	41.16						
TetraEGDME	273	705					8.01	32.90						
EGMEE	273	569	2.44	9.72									5.22	42.26
DEGME	273	630	1.81	10.67									3.44	41.92
DEGMEE	273	656	3.30	9.68									4.46	21.21

Since it was not found a significantly better association scheme in order to improve the description of the liquid and vapour phase density of the glymes, the one initially proposed was then used for the rest of the work.

Another approach was also tested with soft-SAFT, where the adjustment of new molecular parameters was carried out by fitting first order properties (density and vapour pressure) and including also a derivative property (heat capacity). This will be discussed below in the section

4.4 (Extending Soft-SAFT EoS accuracy using heat capacity to enhance the molecular parameters determination).

### 3.2. Group Contribution description of heat capacities

Regardless the EoS importance, their complexity in the description of the compounds pure properties hampers their use. Group contribution (GC) methods, due to their inherent simplicity, stand as one of the most interesting approaches when pursuing simple property determination. That stands even more relevant for families of compounds widely studied and for which reliable experimental data is available. In this work, a GC correlation proposed by Růžička and Domalski<sup>[1,2]</sup> was used to predict heat capacities of glycols and glymes. In 1993, Růžička and Domalski proposed a GC method, based on a second-order group additivity method to estimate the heat capacity of pure organic liquids as a function of temperature for temperatures ranging from the compound's melting point to the their normal boiling temperature. The authors tested and critically evaluated data for over 1300 organic compounds<sup>[1]</sup>. Later in 2004, Zábanský and Růžička proposed an amendment to the previous group contribution table by extending the data to over 1800 heat capacities. According to the authors, the new group contribution parameters are more versatile and more accurate than the previous one<sup>[2]</sup> with deviations lower than 1.7% for the majority of the compounds. According to the authors, heat capacities for a wide number of compounds' families, at atmospheric pressure, can be determined using the following equation:

$$\frac{C_p}{R} = \sum_{i=1}^k n_i \Delta c_i \quad \text{Eq. 3.25}$$

$$\Delta c_i = a_i + b_i \frac{T}{100} + d_i \left( \frac{T}{100} \right)^2 \quad \text{Eq. 3.26}$$

where  $R$  is the ideal gas constant ( $R = 8.314472 \text{ J K}^{-1} \text{ mol}^{-1}$ ),  $n_i$  is the number of additivity units of type  $i$ ,  $\Delta c_i$  is a dimensionless value that represents the additivity units of the type  $i$ ,  $k$  is the total number of additivity units in the molecule,  $T$  is the temperature in K and  $a_i$ ,  $b_i$  and  $d_i$  are adjustable parameters. These parameters are presented in Table 3.2.1 for each version of the model.

**Table 3.2.1-** Group contribution parameters and temperature applicability range proposed by Růžička and Domalski<sup>[1]</sup> and Zábanský and Růžička GC method<sup>[2]</sup>.

### 3. Modelling

Zábranský and Růžička GC method (1993)					
	a	b	d	T <sub>min</sub> / K	T <sub>max</sub> / K
<b>C-(3H,C)</b>	3.845200	-0.339970	0.194890	80	400
<b>C-(2H,C,O)</b>	1.459600	1.465700	-0.2714000	135	505
<b>C-(H3,O)</b>	3.845200	-0.339970	0.194890	80	400
<b>O-(2C)</b>	5.03120	-1.571800	0.3786000	130	350
<b>O-(H,C)(diol)</b>	5.2302	-1.5124	0.54075	195	475
<b>O-(H,C)</b>	12.952	-10.145	2.6261	155	505
Růžička and Domalski GC method (2004)					
	a	b	d	T <sub>min</sub> / K	T <sub>max</sub> / K
<b>C-(3H,C)</b>	4.198450	-0.312709	0.178609	85	700
<b>C-(2H,C,O)</b>	0.517007	1.266310	-0.0939713	137	630
<b>C-(H3,O)</b>	3.703440	-1.128840	0.512390	130	380
<b>O-(2C)</b>	6.35342	-0.969836	-0.0378285	130	520
<b>O-(H,C)(diol)</b>	-3.9141	5.3725	-0.72592	153	590
<b>O-(H,C)</b>	16.1555	-11.938	2.85117	153	590
<b>O-(2C)(alcohol)</b>	0.328815	5.50907	-1.45665	273	460

As can be observed the authors, in the GC method amended in 2004<sup>[2]</sup>, propose a new group for alcohol with ether groups (C-O-C). The results and discussion of these two group contribution methods will be present in **Chapter 4**.

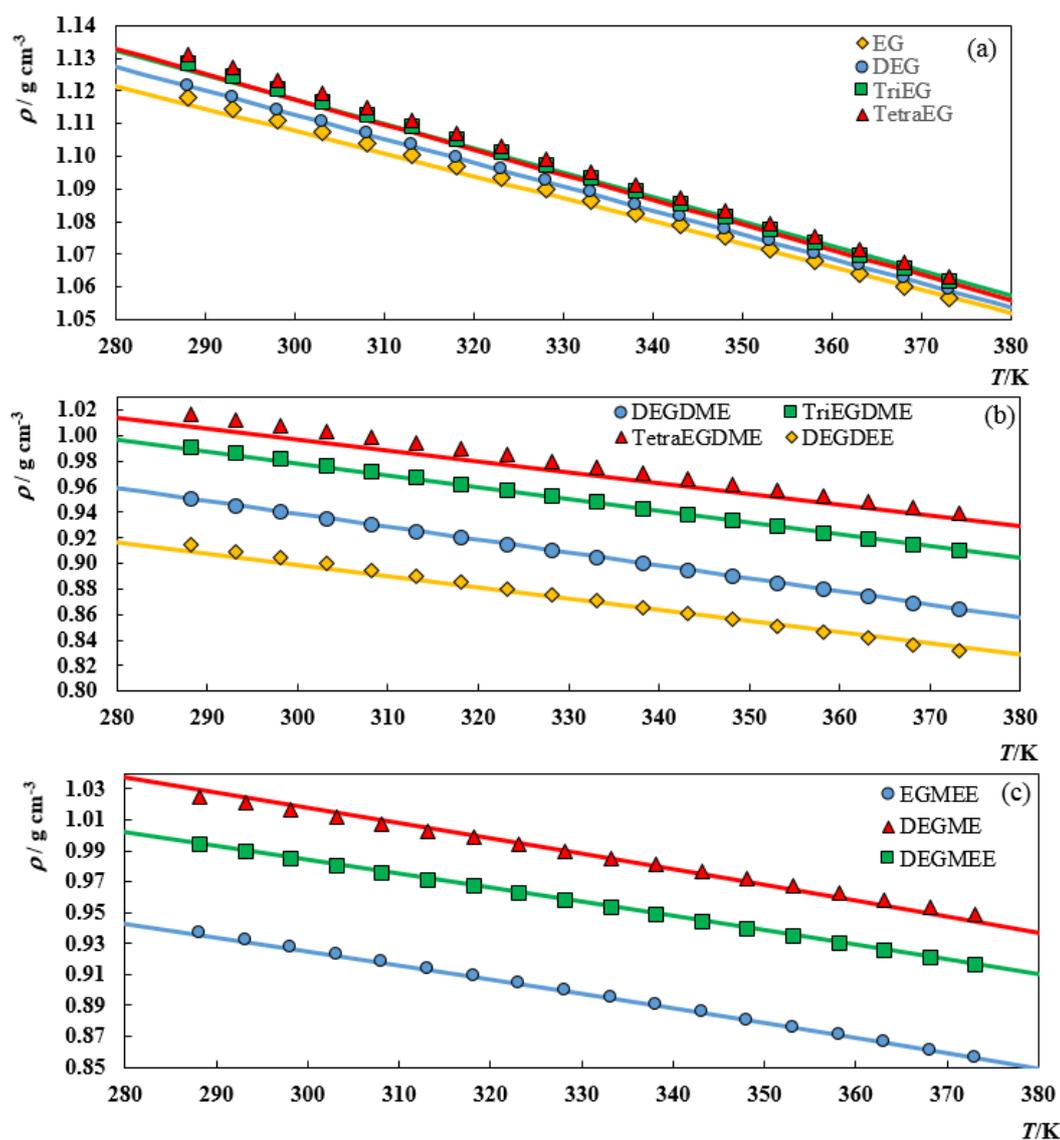
## 4. Results and Discussion



## 4.1. EXPERIMENTAL

### 4.1.1. Density

The density measurements were carried out at atmospheric pressure and in the (288 to 373) K temperature range using the SVM3000 Anton Paar rotational Stabinger viscometer–densimeter. The results are depicted in Figure 4.1.1 and reported in appendix A (Table A.1).



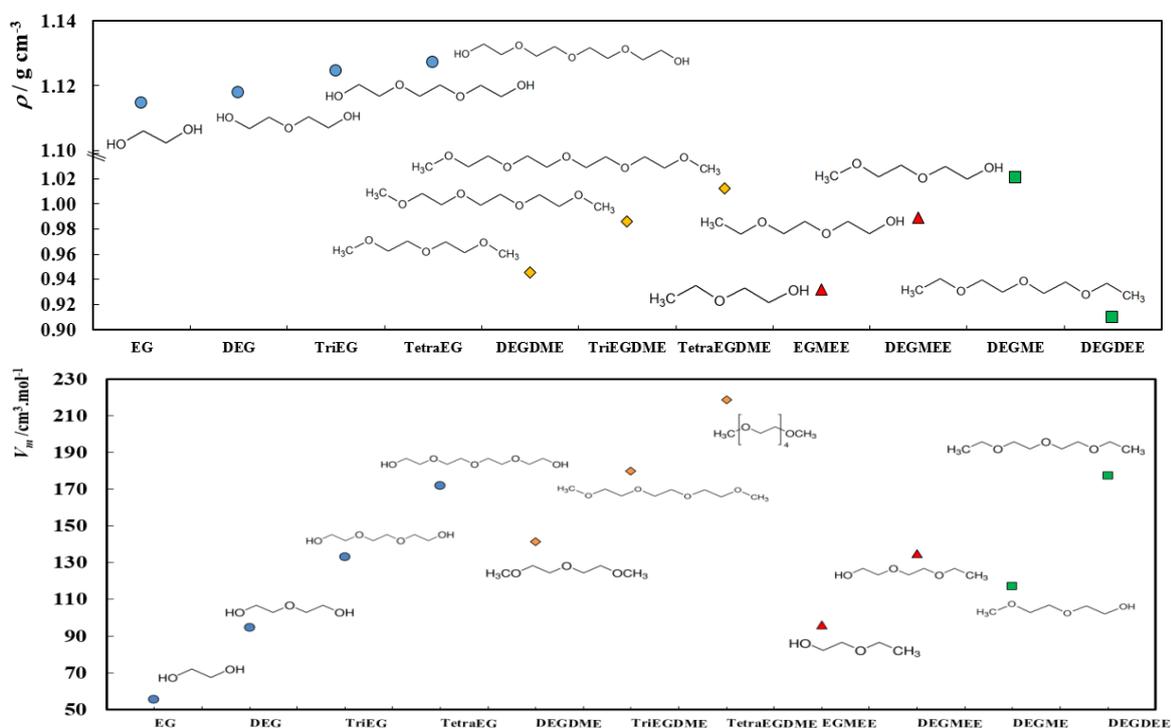
**Figure 4.1.1-** Density as function of temperature of the studied glycols. The solid lines represent the soft-SAFT EoS.

The trends of the density and molar volume for each compound studied are illustrated in Figure 4.1.2.

As depicted in Figure 4.1.2 and as commonly observed for other common organic

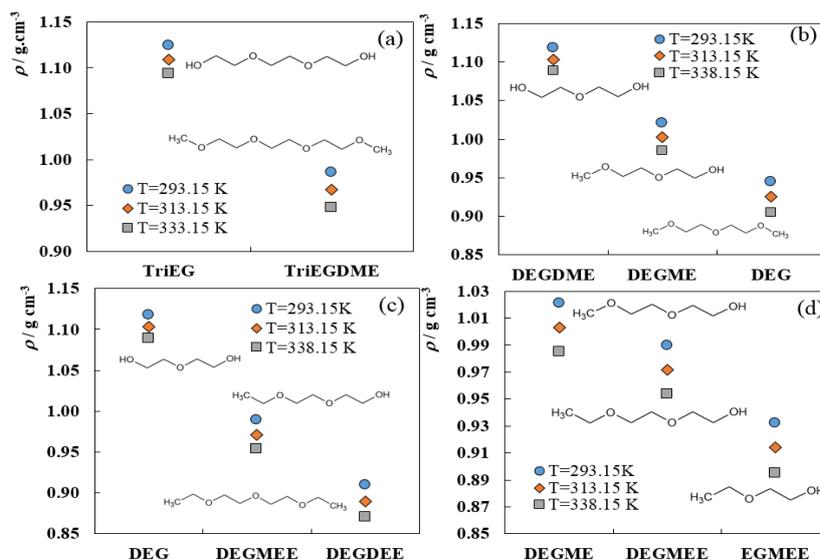
## 4. Results and Discussion

compounds, the glycols densities increase with the number and molar density of the ethoxy groups ( $C_2H_5O$ ). In fact, a molar volume increment of  $38.8 \text{ cm}^3 \text{ mol}^{-1}$  is obtained that corresponds to the molar volume of the ethoxy group. The substitution of a hydrogen of one of the diols hydroxyl groups by a  $CH_3$ , like on the pair DEG–DEGME, leads to a significant decrease on the density, as depicted in Figure 4.1.2 and Figure 4.1.3b. Moreover, even though the substitution of one hydrogen by a  $CH_3$  groups leads to a significant decrease on the density, the substitution of both terminal hydrogens, like on the pairs DEG–DEGDME, TriEG–TriEGDME (Figure 4.1.3a) and TetraEG–TetraEGDME, leads to a slightly higher decrease to that observed to one substitution, as depicted in Figure 4.1.2. Furthermore, in terms of molar volumes the substitution of the hydrogens of the hydroxyl groups lead to a regular increase of  $23.4 \text{ cm}^3 \text{ mol}^{-1}$  that corresponds to the molar volume of the  $CH_3$  group.



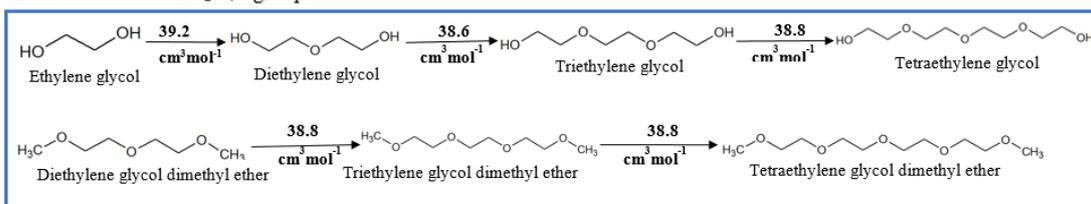
**Figure 4.1.2-** Density (top) and molar volume (bottom) as function of the compounds studied, at 293.15 K

By the other hand, changing the hydrogen atom from the hydroxyl terminal group ( $-OH$ ) by an ethyl group ( $-C_2H_5$ ) leads to a higher decrease on the density than that observed by adding a  $CH_3$  group, like in the cases of DEG to DEGMEE and DEGMEE to DEGDEE (Figure 4.1.3c). Nonetheless, for the molar volume this decrease is less pronounced with the ethyl substituted compounds presenting higher molar volumes than methyl substituted ones, due to the increment of the  $CH_2$  group that leads, as expected, to an increase of  $18.1 \text{ cm}^3 \text{ mol}^{-1}$  due to the group molar volume.

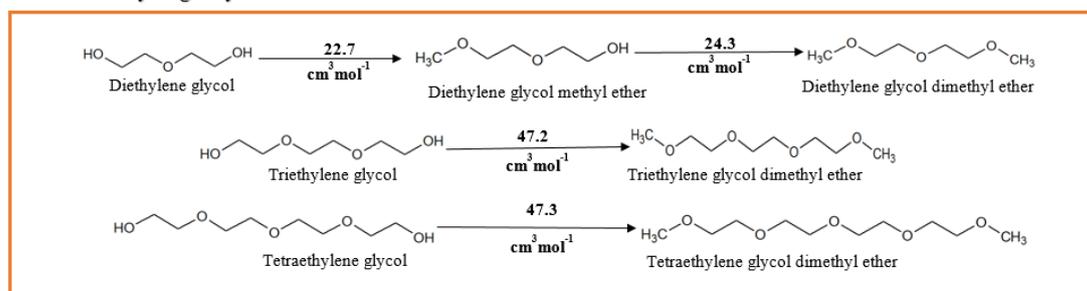


**Figure 4.1.3-** Density in function of :triethylene glycol dimethyl ether and triethylene glycol (a); Diethylene glycol dimethyl and methyl ether and diethylene glycol (b); ethylene glycol, diethylene glycol mono- and di- ethyl ether (c); diethylene glycol mono –methyl, -ethyl diether and ethylene glycol monoethyl ether (d).

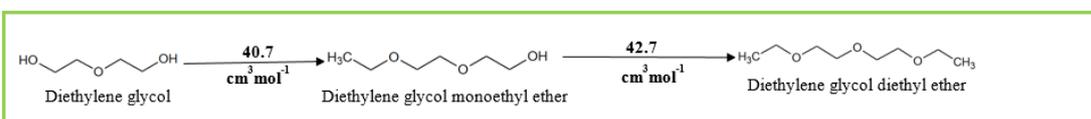
#### Effect of number of C<sub>2</sub>H<sub>4</sub>O group



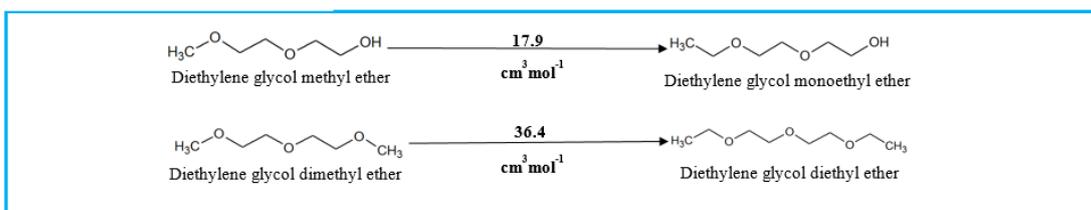
#### Effect of OH hydrogen by CH<sub>3</sub>



#### Effect of OH hydrogen by C<sub>2</sub>H<sub>5</sub>



#### Effect of CH<sub>2</sub>



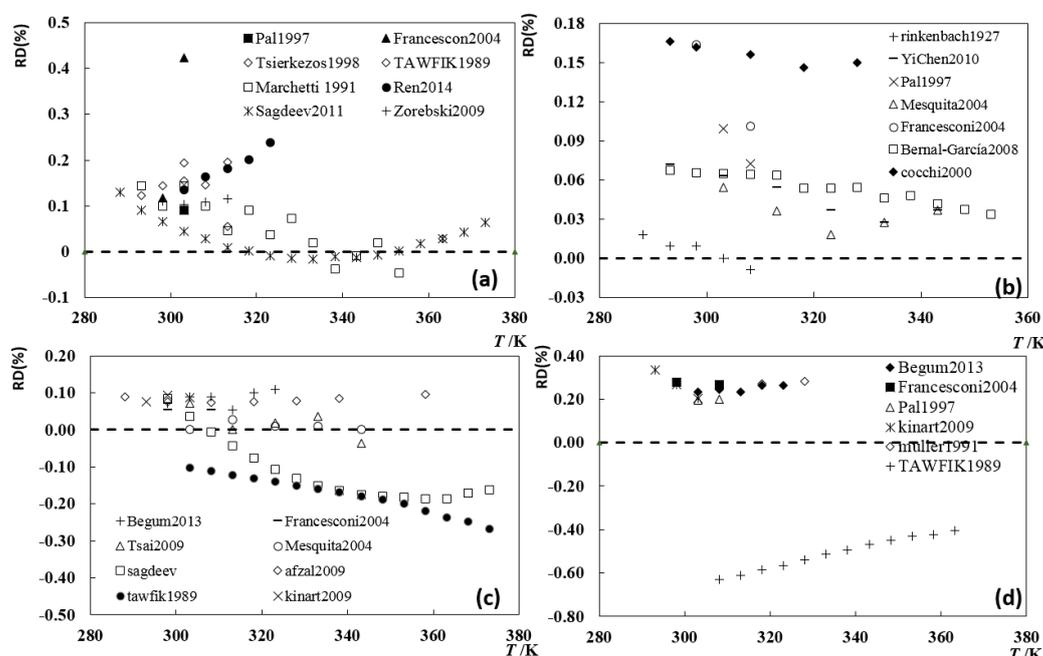
**Figure 4.1.4-** Impact of the molecular structure on density at 293.15 K and atmospheric pressure.

## 4. Results and Discussion

Glycols and glymes are a class of compounds widely studied in the literature<sup>[12,14,17–19,23,26,41,74,82–85,87–119]</sup>. Nevertheless, even though the density for some of these compounds is well established in the literature, some present significant discrepancies among various authors. Thus, the data here measured was compared against that available in the literature<sup>[12,14,17–19,23,26,41,74,82–85,87–119]</sup>. As depicted in Figure 4.1.5 through Figure 4.1.7 the data reported here presents small relative deviations towards the literature values.

For ethylene glycol the deviations and the discrepancies between authors are not significant. As an example, the data set of Marchetti et al.<sup>[89]</sup> and Sagdeev et al.<sup>[84]</sup> for EG agrees with our experimental data values within a %AAD of 0.06% and 0.03%, respectively. The remaining data, even though the overall %AAD is below 0.15%, present higher deviations towards our data, but still with a %AAD of 0.42%.

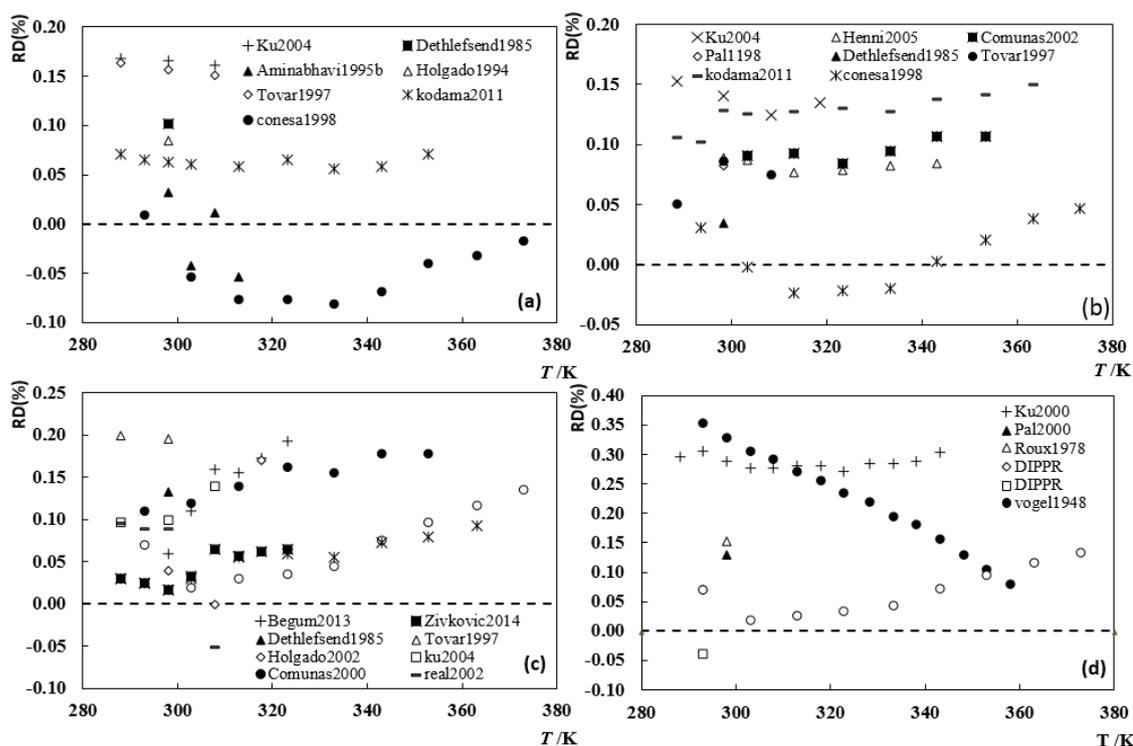
For diethylene glycol, a %AAD of 0.05% against the data of Bernal-Garcia et al.<sup>[93]</sup> is observed. As shown in Figure 4.1.5b, large deviations against the data of Cocchi et al.<sup>[92]</sup> are observed, with a %AAD of 0.16%. These deviations seem to be related not to the apparatus and methodology used, but due to the author's high water content for the compound. Figure 4.1.5c, for triethylene glycol, shows a good agreement between our data and the data of most of the authors. The only exception is the deviations observed against the data of Tawfik et al.<sup>[88]</sup> and Sagdeev et al.<sup>[84]</sup> that present %AAD of 0.17% and 0.16%, respectively.



**Figure 4.1.5-** Relative deviations between experimental density of this work and those reported in the literature<sup>[19,23,84,87–98]</sup> for a) EG b) DEG c) TriEG and d) TetraEG.

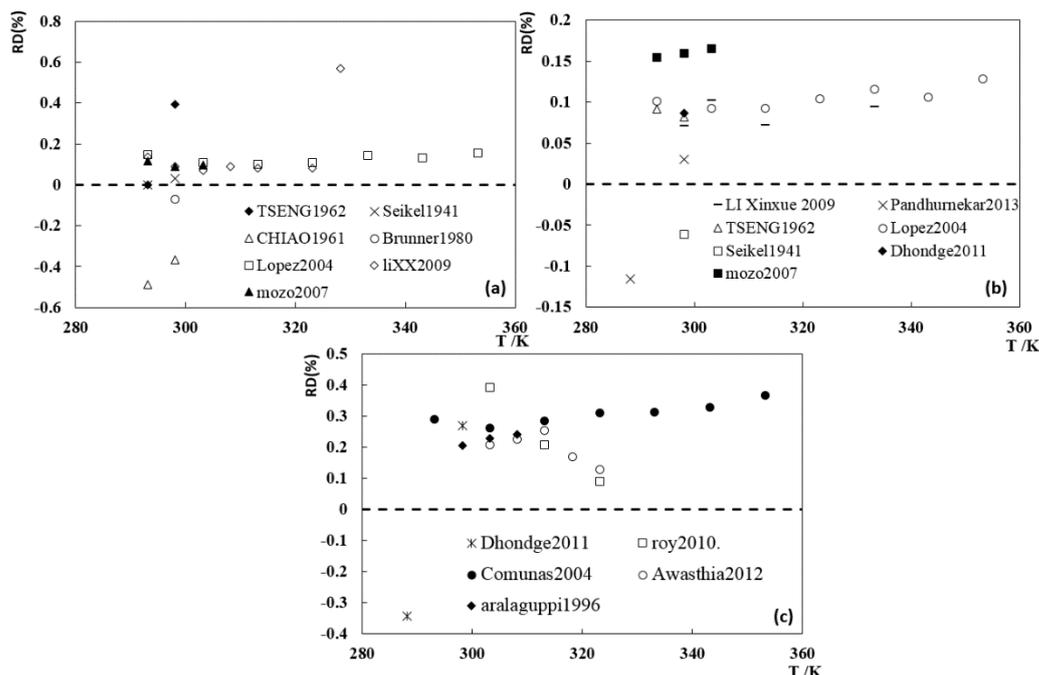
For the glycols studied the highest deviations were found for the tetraethylene glycol, as depicted in Figure 4.1.5d. In fact, average deviations of 0.27% against the data of Muller et al.<sup>[90]</sup>, Begum et al.<sup>[83]</sup> and Kinart et al.<sup>[19]</sup> and -0.50% against the data of Tawfik et al.<sup>[88]</sup> can be found. These higher deviations can be related to the absence of purification procedures implemented by the authors and therefore, to the presence of impurities like small traces of water.

For the last group of glycols, containing only one hydroxyl terminal group, the discrepancies between our data and that of the literature<sup>[12,14,17,18,26,41,74,82,83,85,99–119]</sup> are depicted in Figure 4.1.7. Contrary to the previous compounds, data for glymes are scarcer and deviations that range from -0.48 % to 0.56% can be found. Nonetheless, if one clearly removes data that present significant discrepancies among authors, like the case of LiX et al.<sup>[13]</sup> and Chiao et al.<sup>[100]</sup>, for diethylene glycol methyl ether, smaller discrepancies, with %AAD of 0.015%, are observed. Similar to that observed for the glycols in Figure 4.1.5, the alkyl chain increase lead to higher deviations, like in the case of ethylene glycol monoethyl ether with %AAD of 0.31%.



**Figure 4.1.6-** Relative deviations between experimental density of this work and those reported in the literature<sup>[14,17,26,74,83,85,107–119]</sup> for diethylene glycol dimethyl ether (a), triethylene glycol dimethyl ether (b), tetraethylene glycol dimethyl ether (c) and diethylene glycol diethyl ether (d).

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**Figure 4.1.7-** Relative deviations between experimental density of this work and those reported in the literature<sup>[12,18,41,82,99–106]</sup>, (a) diethylene glycol methyl ether, (b) diethylene glycol monoethyl ether and (c) ethylene glycol monoethyl ether.

As depicted in Figure 4.1.5 through Figure 4.1.7 and discussed above no significant or systematic deviations between the density measured here and that reported in the literature<sup>[12,14,17,18,26,41,74,82,83,85,99–119]</sup> can be found, denoting the quality of the data measured here.

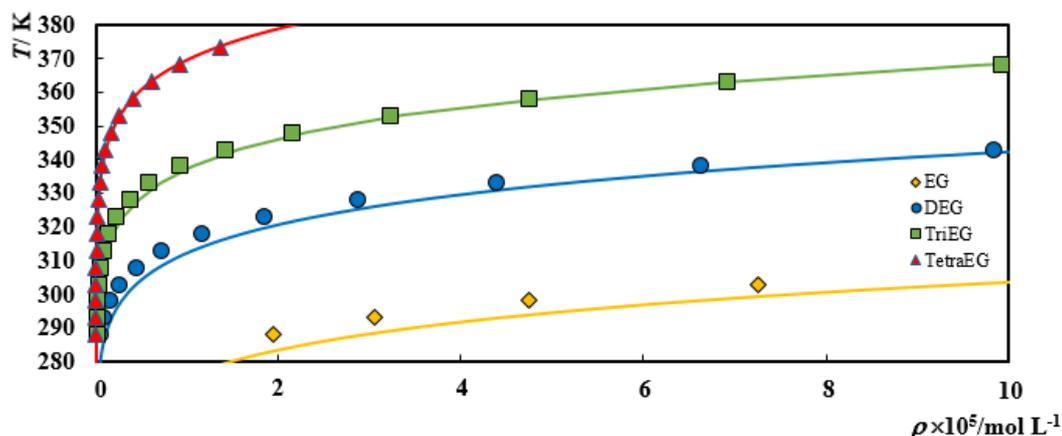
Regarding now the deviations between our experimental data and that from soft-SAFT, it can be seen, with the data reported in Table 4.1.1, that the liquid density are well described by soft-SAFT within the temperature range of the experimental measurements, with a maximum %AAD of 0.27% and 0.23% for tetraethylene glycol dimethyl ether and diethylene glycol methyl ether, respectively. Moreover, the %AAD for all the compounds studied is 0.12% which is in the same order of the deviations reported within the literature data.

**Table 4.1.1-** Percentage absolute average deviation between the experimental and soft-SAFT liquid and vapour phase density at equilibrium condition.

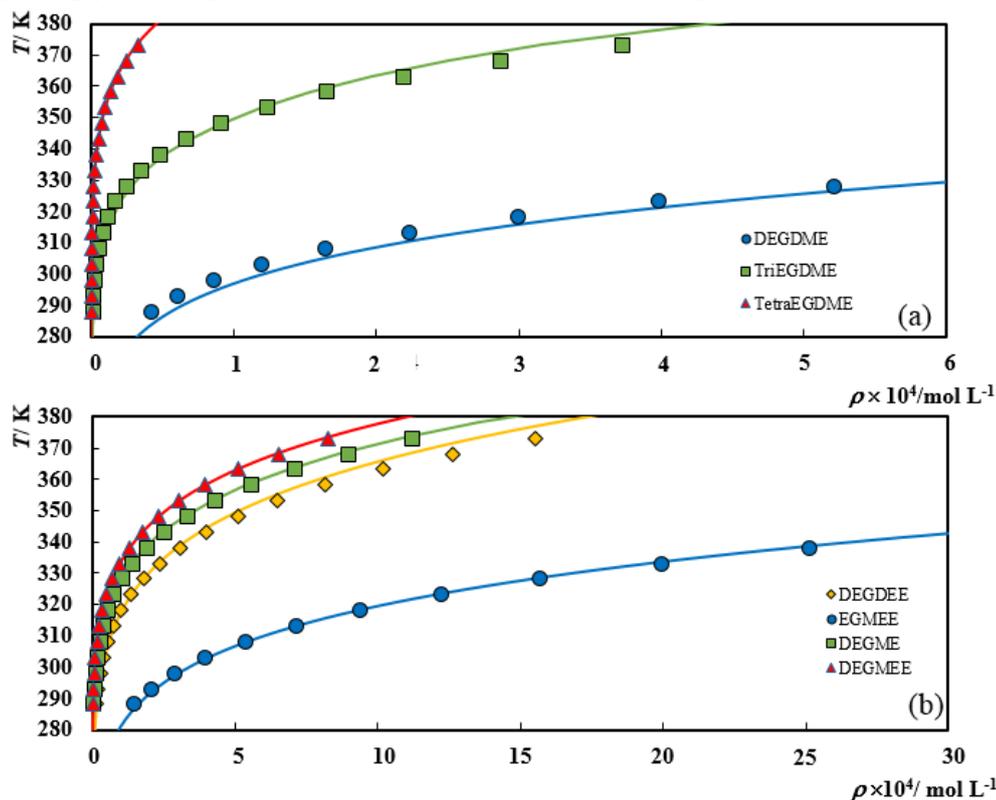
Compound	EG	DEG	TriEG	TetraEG	DEGDME	DEGDEE	TriEGDME	TetraEGDME	EGMEE	DEGMEE	DEGME
<b>Density liquid phase</b>											
$\Delta\rho_{\max} \times 10^2$ (mol L <sup>-1</sup> )	3.75	0.38	1.53	2.35	0.63	2.94	0.89	4.32	1.23	0.76	3.59
%AAD	0.11	0.02	0.09	0.07	0.06	0.26	0.09	0.27	0.05	0.08	0.23
<b>Density vapour phase</b>											
$\Delta\rho_{\max} \times 10^5$ (mol L <sup>-1</sup> )	6.17	0.95	0.07	0.00	22.55	20.50	5.62	0.12	9.11	0.70	3.48
%AAD	17.48	37.98	33.72	33.00	10.74	6.78	24.89	26.25	2.75	3.10	2.91

Looking now in more detail to the vapour phase density it can be observed that soft-SAFT EoS is able to predict the property, as illustrated in Figure 4.1.8 and Figure 4.1.9.

It is worth mention that despite the errors obtained, with %AAD between 33% and 38% for di, tri and tetraethylene glycol as reported in Table 4.1.1, are high, they are due to the magnitude of the density values ( $1 \times 10^{-5}$ ). Nonetheless, the maximum molar density differences observed are  $\Delta\rho_{max}=22.55 \times 10^{-5}$  (mol. L<sup>-1</sup>).



**Figure 4.1.8-** Temperature as function of vapour phase molar density for mono, di, tri and tetraethylene glycol, at equilibrium condition and the solid lines represent the soft-SAFT results.

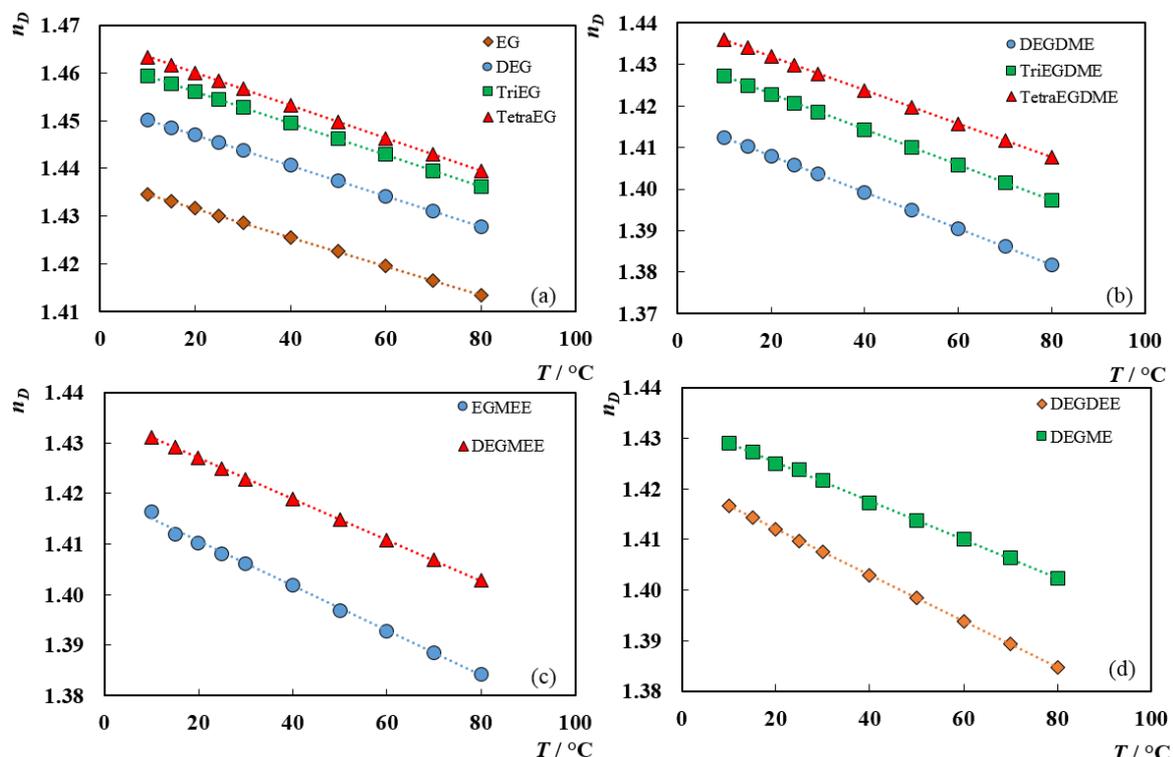


**Figure 4.1.9-** Temperature as function of vapour phase molar density for glymes (a) and glycol ethers (b) here, at equilibrium condition and the solid lines represent the soft-SAFT results.

## 4. Results and Discussion

### 4.1.2. Refractive index

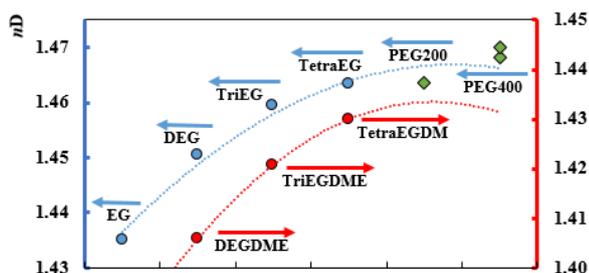
The refractive indices were measured at atmospheric pressure within the (283.15-353.15) K temperature range, as reported in the appendix A (Table A.2) and depicted in Figure 4.1.10.



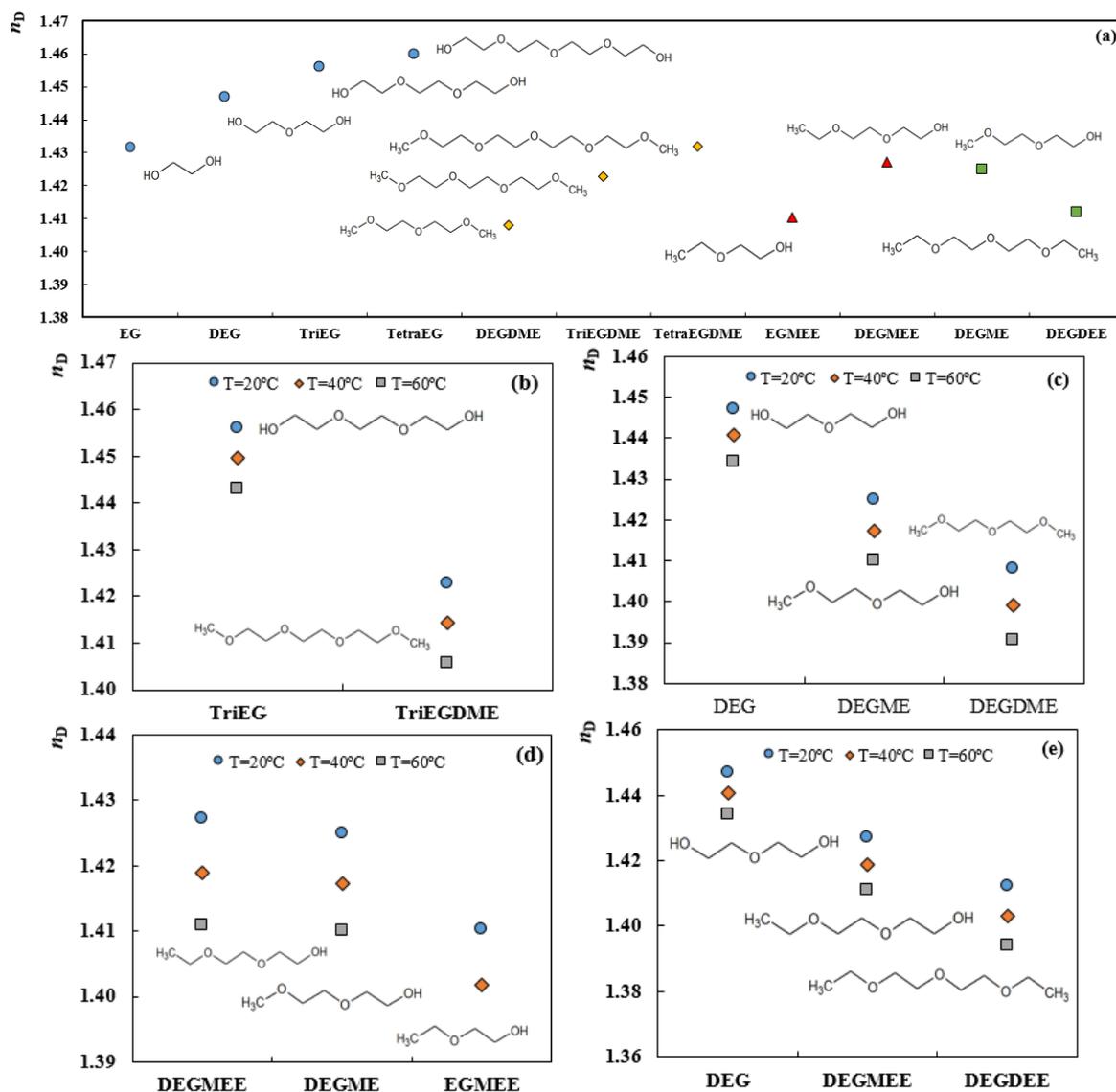
**Figure 4.1.10-** Refractive index as a function of temperature for the compounds studied. The dashed lines are guides for the eyes.

As commonly observed the refractive index decreases with the temperature increase, and for the glycols studied it is no different, denoting a higher velocity of light in the medium as the temperature increases.

Based on Figure 4.1.12a the effect of increasing the number of ethoxy groups can be analysed, showing that the glycols (diols) and glymes chain length increase leads to an increase of the refractive index. Contrary to what is observed for the molar volumes, where the increase of the number of ethoxy groups lead to a constant increase of the molar volumes, here the increase of the number of ethoxy groups lead to an increase of the refractive index that seems to converge to a constant value. In fact, if one plots the refractive indices of different molecular weight PEGs (polyethylene glycols), namely PEG200 and PEG400, this behaviour is easier observed, as depicted in Figure 4.1.11.



**Figure 4.1.11**-The number of ethoxy group effect in glycols, glymes, PEG200<sup>[120]</sup> and PEG400<sup>[120,121]</sup> on the refractive index at 298.15 K.



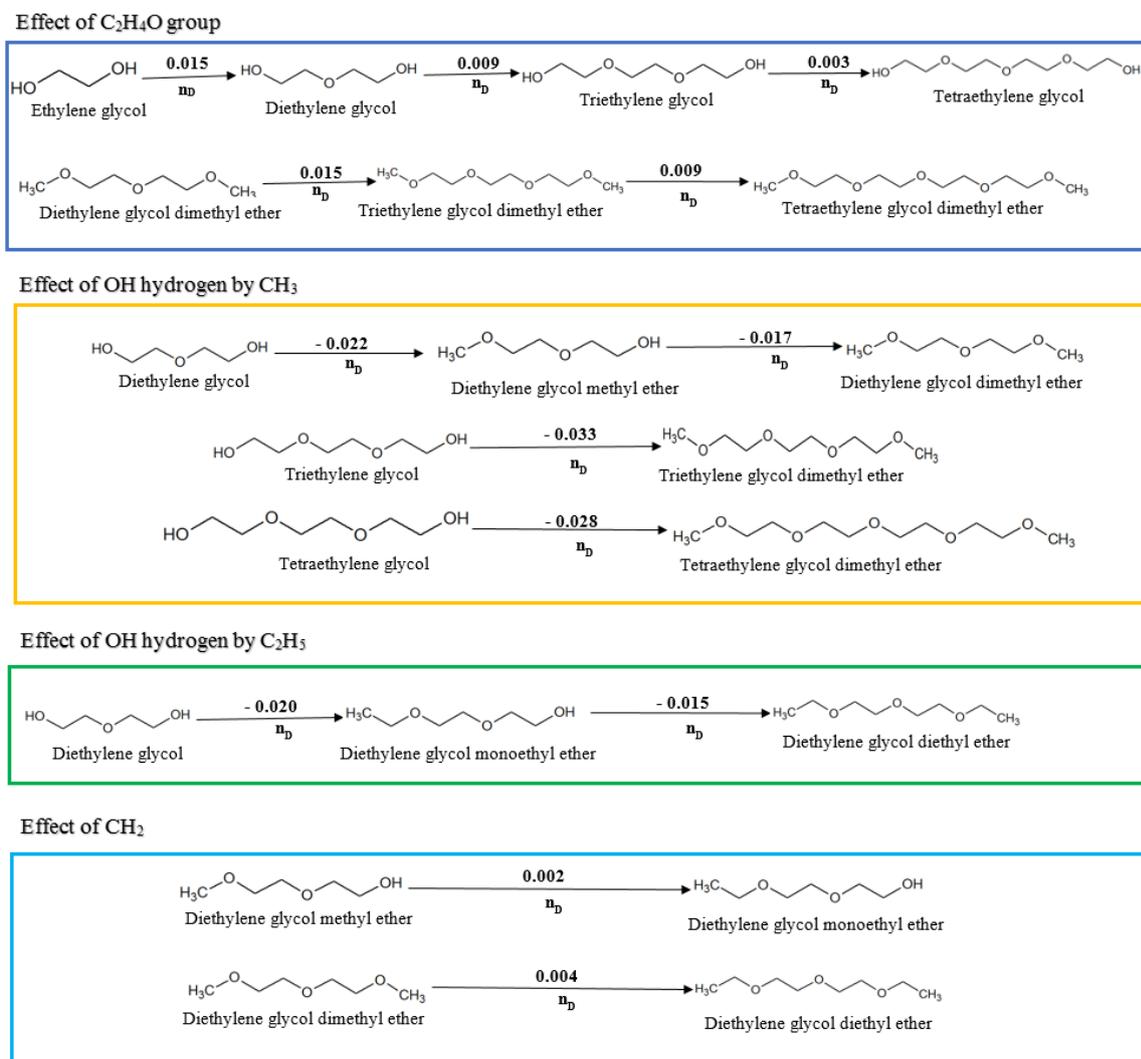
**Figure 4.1.12**- Refractive index as function of glycols molecules at 293.15 K, at atmospheric pressure (a); Refractive index in function of: triethylene glycol dimethyl ether and triethylene glycol (b); Diethylene glycol dimethyl and methyl ether and diethylene glycol (c); diethylene glycol mono ethyl ether, diethylene glycol methyl ether and ethylene glycol mono ethyl ether (c); Diethylene glycol, diethylene glycol mono and diethyl ether (d).

Looking now, for the effect of replacing one hydrogen of the hydroxyl by a methyl group

#### 4. Results and Discussion

like the pair DEG-DEGME or DEGME to DEGDME, represented in Figure 4.1.12c, regular decrease of  $0.02 n_D$  is observed. In the same manner, the substitution of both the diols hydroxyl groups by  $\text{CH}_3$  groups, like in the case of DEG-DEGDME, TriEG-TriEGDME (Figure 4.1.12b) and TetraEG-TetraEGDME lead also to a decrease of the refractive index. In fact, the refractive index of these compounds present a regular increase of  $0.04 n_D$ , that correspond to the addition of two  $\text{CH}_3$  groups ( $\text{CH}_3=0.02 n_D$ ).

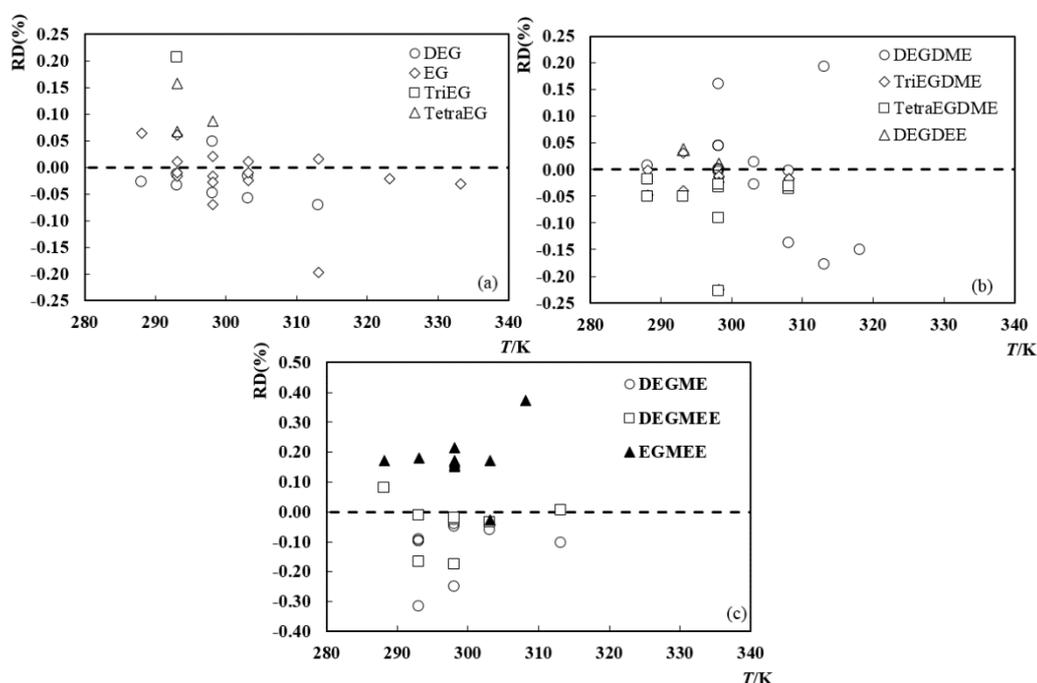
The substitution of an ethyl group, rather than a methyl group, leads to a slight lower decrease of the refractive index, as illustrated in Figure 4.1.12a with the pairs DEG-DEGME and DEG-DEGMEE. Furthermore, the difference observed between the glycols methyl ethers and glycols ethyl ether, like the DEGME and DEGMEE, and the glycols dimethyl ethers and glycols diethyl ethers, like in DEGDME and DEGDEE, correspond to an increase of  $0.02 n_D$  that corresponds to the contribution of the  $\text{CH}_2$  group.



**Figure 4.1.13-** Impact of the molecular structure on refractive index at 293.15 K and atmospheric pressure.

Even though refractive indices are not as widely reported as densities for some compounds literature data is available. Seikel et al.<sup>[99]</sup> reported refractive indices for diethylene glycol methyl ether and Pandhurnekar et al.<sup>[106]</sup> reported for diethylene glycol monoethyl methyl ether. The refractive indices previously reported in the literature<sup>[12,16,17,22,26,28,30,31,41,82,89,91,98,100,107,115,118,122–130]</sup>, plotted in Figure 4.1.14 show that the refractive index between the authors data and ours present small deviations. The most significant deviations identified are for ethylene glycol monoethyl ether, with %AAD of 0.36% against the data of Aralaguppi et al.<sup>[82]</sup>.

Based on this analysis, it can be stated that the experimental refractive indices determined are in good agreement with the data previously reported in literature and that small, no systematic, deviations are observed.



**Figure 4.1.14-** Percentage relative deviations as functions of temperature for the studied compounds<sup>[12,16,17,22,26,28,30,31,41,82,89,91,98–100,106,107,115,118,122–130]</sup>: a) EG, DEG, TriEG) and TetraEG; b) DEGDME, TriEGDME, TetraEGDME and DEGDEE; c) DEGME, DEGMEE and EGMEE.

### 4.1.3. Viscosity

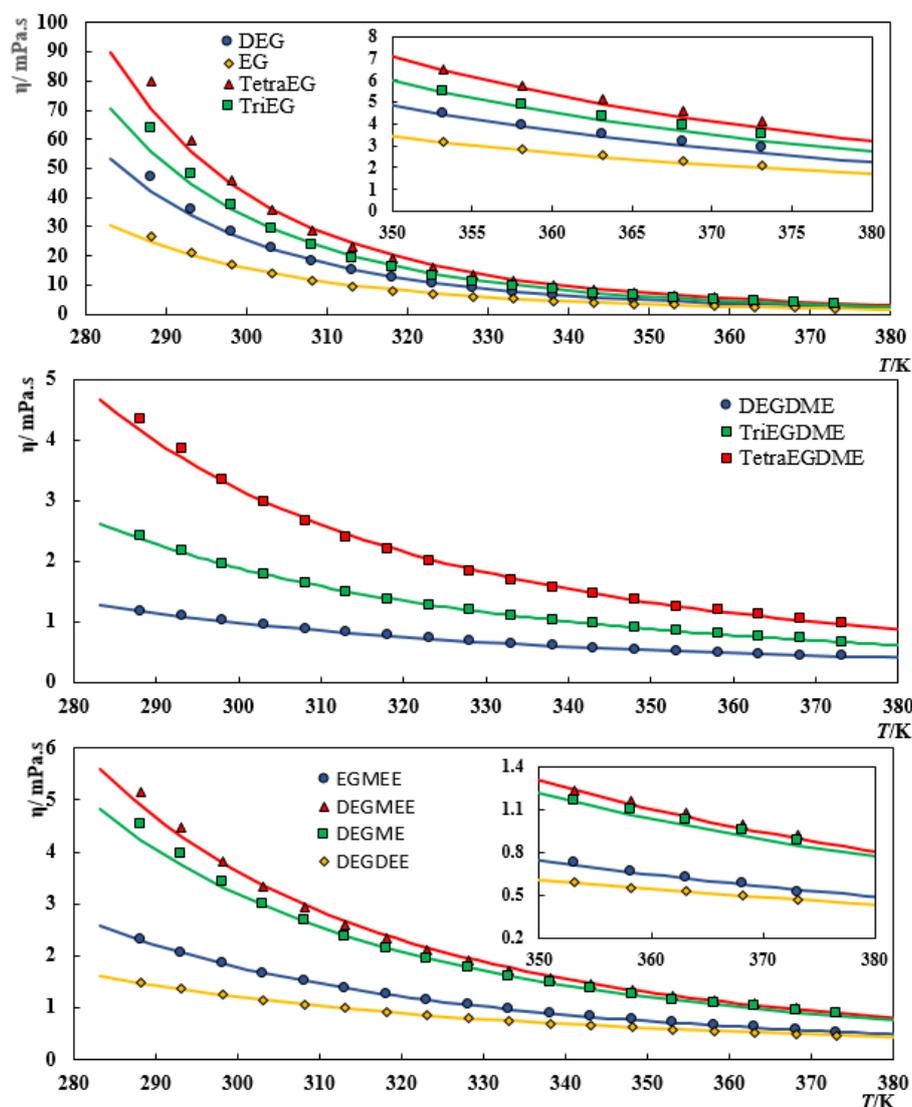
The viscosity of glycols was determined in the (288.15 to 373.15) K temperature range and at atmospheric pressure, as reported in appendix A (Table A.3) and depicted in Figure 4.1.15. As commonly observed, the viscosity decreases as the temperature increases.

Similar to the study done for density and refractive index the influence of different groups was investigated. As depicted in Figure 4.1.16, the increase of the number of ethoxy

#### 4. Results and Discussion

groups leads to the increasing of the viscosity. Comparing the difference of the viscosity between the pairs DEG-EG, TriEG-DEG and TetraEG-TriEG, the differences values are 14.8, 12.0, and 11.6mPa.s at 293.15 K, respectively. For glymes, the effect of having more ethoxy group in the molecule increase also the viscosity, but here, the effect is less substantial.

On the other side, the substitution of hydrogen of one of the diols hydroxyl groups by a  $\text{CH}_3$ , like on the pairs DEG-DEGME, leads to a significant decrease on the viscosity(32.0 mPa.s), as depicted in Figure 4.1.17a. Although the replacing of one hydrogen by  $\text{CH}_3$  leads to a significant decrease, the substitution of both terminal hydrogens, like on the pairs DEG-DEGDME, TriEG-TriEGDME (Figure 4.1.17b) and TetraEG-TetraEGDME, give a slight higher decrease to that observed to one substitution. Nonetheless, it was observed a non-regular difference between the pairs (35.0, 45.9 and 55.8) mPa.s at 298.15 K, respectively.

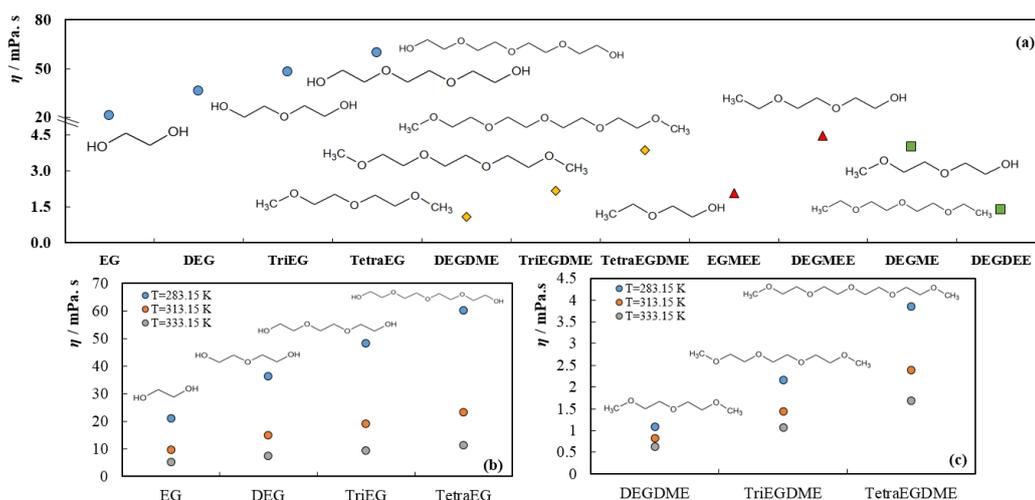


**Figure 4.1.15-** Viscosity as a function of temperature for the studied compounds. The solid lines are the soft-SAFT EoS results.

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The substitution of one ethyl group instead of a methyl, lead also to a slight decreasing on the viscosity with the pairs DEG-DEGMEE (31.6 mPa.s). Moreover, the differences analysed between for glycols mono methyl and ethyl ethers, like DEGME and DEGMEE, and the glycols dimethyl ethers and glycols diethyl ethers, like the DEGDME and DEGDEE, correspond to an increase of 0.22 that corresponds to the contribution of the CH<sub>2</sub> group.

To summarize, the increase of the molecular chain, and the number of ether groups, together with or without the terminal hydroxyl groups imposing a higher entanglement to the compounds and therefore, also an increase on the viscosity. This behaviour is commonly observed for other organic molecules like alkanes and alcohols<sup>[125]</sup>. The effect of replacing the hydroxyl group hydrogen by a CH<sub>3</sub> or C<sub>2</sub>H<sub>5</sub> group, in the glycols, it can be seen a decrease of one order of magnitude on the viscosity. This behaviour highlights the relevance and the impact of the molecules' hydrogen bonds on the viscosity and denotes the enthalpic effects overpowering the entropic. The values of these effects studied are reported in figure *Figure 4.1.17*.



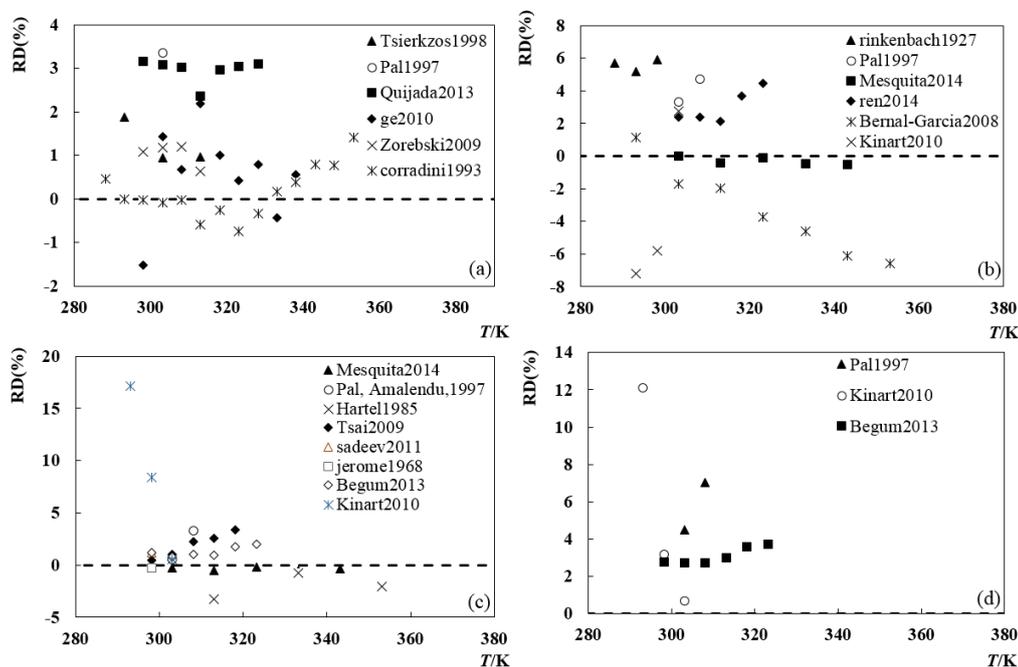
**Figure 4.1.16-** Viscosity as function of glycols molecules at 293.15 K, at atmospheric pressure (a); Viscosity in function of: mono, di, tri and tetraethylene glycol (b); die, tri and tetraethylene glycol dimethyl ethers(c).



volume, and with that conclude that refractive index and viscosity are not properties with an “additive” trend.

Viscosity is one of the properties most evaluated in the literature. However, even though widely available, the viscosity data in the literature are often reported for temperatures outside of the range investigated here or measured at a single temperature aiming not to accurately determine the property value but to obtain a value to be used on calculations, for which high accuracy was not relevant. That being said, one could expect high deviations not only among authors but towards our data. However, overall small deviations are also observed, as depicted in Figure 4.1.19, Figure 4.1.20 and Figure 4.1.21. The only exception are the deviations observed towards the data of Kinart et al.<sup>[131]</sup> that present the largest deviations observed (around 12%).

The remaining compounds present deviations within  $\pm 6\%$ . Ethylene glycol presents average deviations within  $\pm 2.0\%$ , with the exception of the data from Quijada et al.<sup>[132]</sup> and Pal et al.<sup>[23]</sup> that reported viscosities using a suspended level Ubbelohde viscometer (capillary viscometer) that deviate 3.1% from ours. These deviations seem related to the apparatus and methodology adopted since comparing the authors data with that of Corradini et al.<sup>[133]</sup> measured using a similar equipment a %AAD of 0.4% is observed.



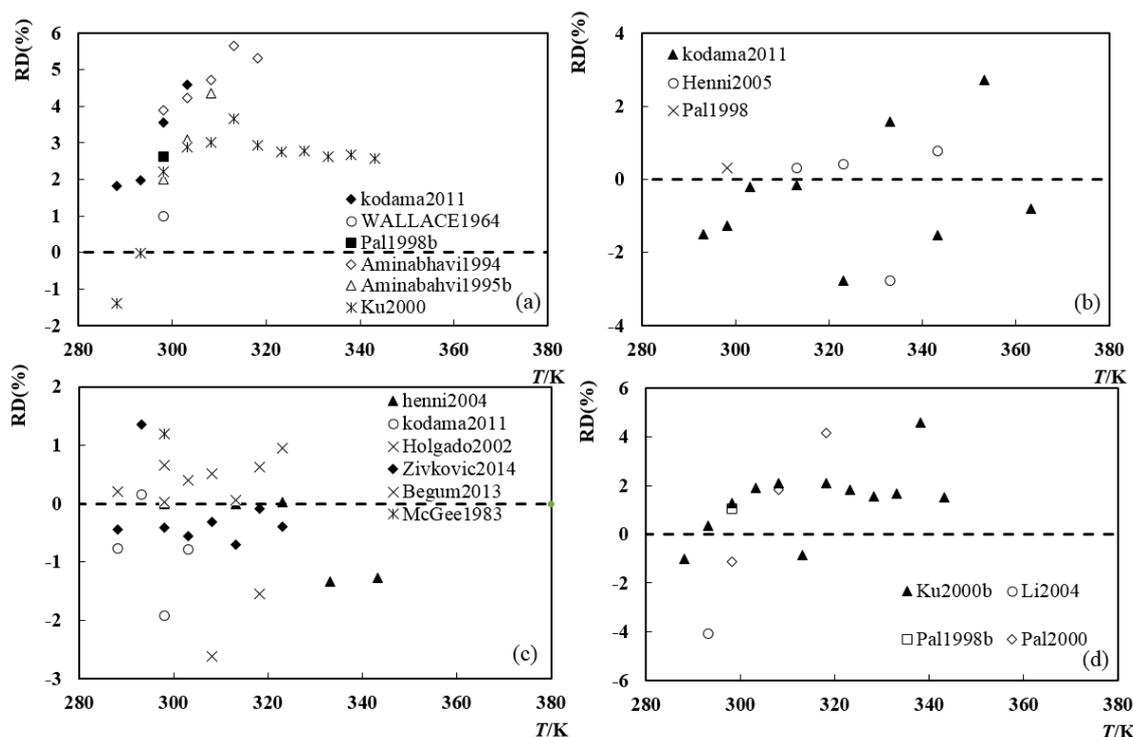
**Figure 4.1.19-** Relative deviations between this work’s experimental data and data available in the literature as a function of temperature<sup>[20,23,83,84,86,91,93,94,96–98,131–135]</sup> : a) EG, b) DEG, c) TriEG and d) TetraEG.

For di and triethylene glycol Mesquita et al.<sup>[96]</sup> reported viscosities, using a similar

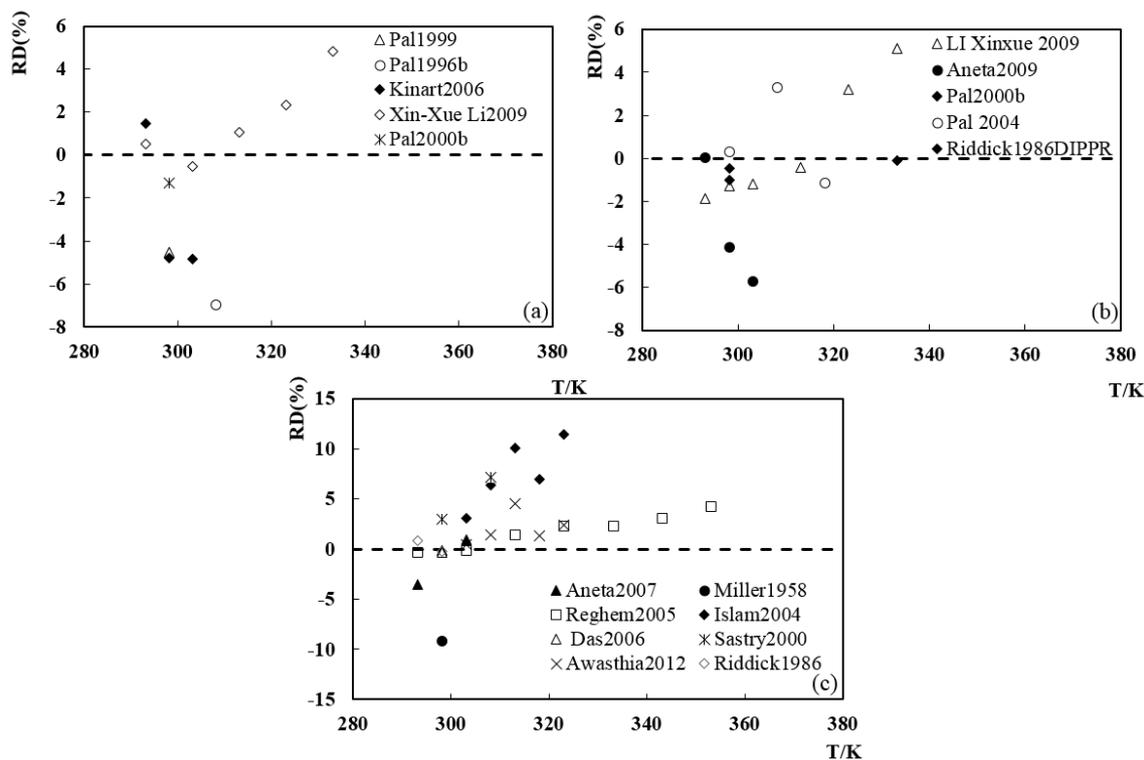
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apparatus to ours, that are in very good agreement towards those here measured, as shown in Figure 4.1.19b and Figure 4.1.19c. On the other hand, higher deviations towards the data of Kinart et al.<sup>[131]</sup> are observed for di-, tri- and tetraethylene glycol. Similar to the case of ethylene glycol and the data of Queijada et al.<sup>[132]</sup> and Pal et al.<sup>[23]</sup> the authors<sup>[97,136]</sup> also used an Ubbelohde capillary viscometer that, together with the absence of a purification step, might have to the higher, nonetheless small, deviations. For tetraethylene glycol the experimental data available in the literature is limited, but those available present small deviations towards ours, as shown in the Figure 4.1.19d.

Despite of the viscosity measurements' sensibility to impurities, especially to even small traces of water, the discrepancies observed are not significant. Overall, our experimental data are concordant with that reported in the literature with a maximum relative deviation of 5.6% for the case of diethylene glycol dimethyl ether from Aminabhavi et al.<sup>[107]</sup>.



**Figure 4.1.20-** Relative deviations between this work's experimental data and viscosity data available in the literature<sup>[13,16,22,26,31,83,85,107,112–114,118,137–139]</sup> as a function of temperature for glycols: a) DEGDME, b)TriEGDME, c) TetraEGDME and d) DEGDEE.



**Figure 4.1.21-** Relative deviations between this work's experimental viscosity data and that available in the literature<sup>[21,24,27,74,104,105,122,140–146]</sup> as function of temperature: a) DEGME, b) DEGMEE and c) EGMEE.

## 4.2. MODELLING

### 4.2.1. Heat capacity prediction by a group contribution method

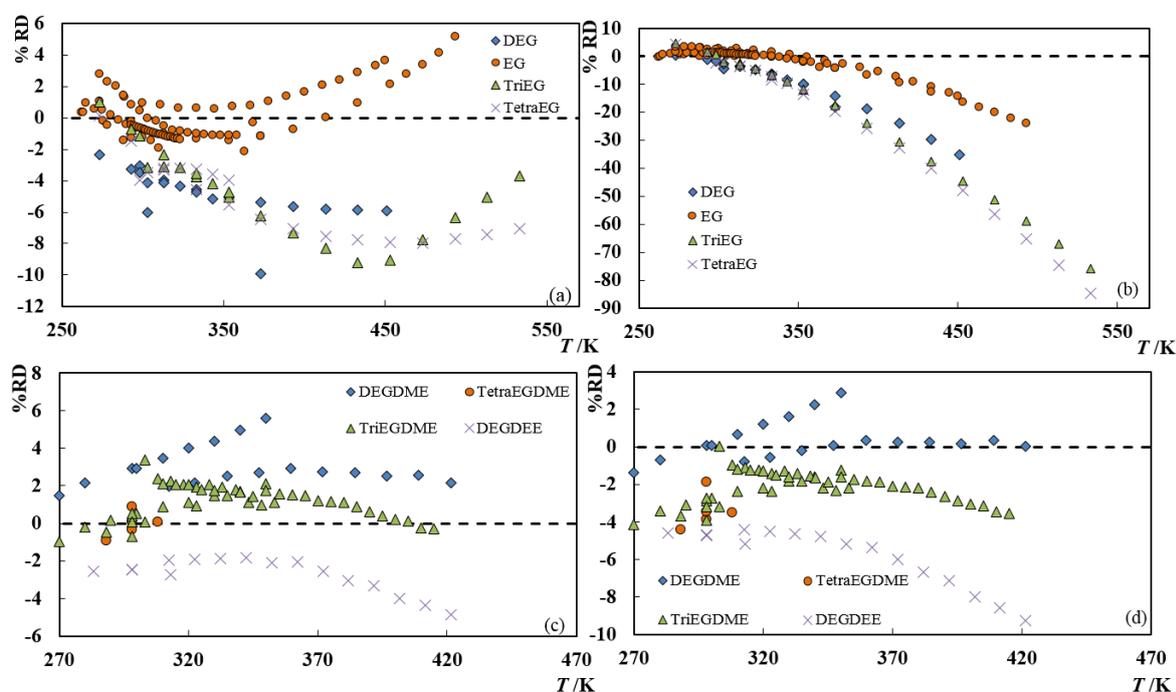
Since in this work, it was not possible to measure the heat capacity of glycols, for that reason we used two group contribution methods in order to evaluate the experimental data available in the literature. Group contribution methods are, probably, the most extensive and widely available and stand as a simple method (set of simple equations and heuristics) to calculate the compounds properties. In this work one group contribution method<sup>[1,2]</sup> for the estimation of heat capacities was evaluated. The group contribution method proposed by Růžička and Domalski<sup>[1]</sup> and later amended, extending the group contribution table to over 500 heat capacities, by Zábanský and Růžička<sup>[2]</sup> was used to predict the compounds here studied heat capacities. Furthermore, both versions of the group contribution method were evaluated. The results of that evaluation are plotted in Figure 4.2.1 and Figure 4.2.2 where the relative deviations between experimental data and data estimated by the group contribution method, as a function of temperature, are depicted. Each figure is organized as follows: the left side plots represent the applicability of the Růžička and Domalski<sup>[1]</sup> GC method and the right side plots the GC method version amended by Zábanský and Růžička<sup>[2]</sup> For the use of the GC method

## 4. Results and Discussion

literature data, used also in Chapter 4 Extending Soft-SAFT EoS accuracy using heat capacity to enhance the molecular parameters determination, was gathered comprising heat capacities within 535 and 139 J mol<sup>-1</sup> K<sup>-1</sup> in the (209 - 533) K temperature range.

It is worth noting that contrary to density, viscosity and refractive indices, discussed before, important discrepancies among data from different authors is observed, as depicted in Figure 4.5.1 and 4.5.2. Thus, and emphasizing that the data quality evaluation stand out of the scope of this thesis, only a discussion based on the predictive ability of the GC method will be given. As depicted in Figure 4.2.1 and Figure 4.2.2 the two versions of the GC method provide results significantly different. Striking is the fact that the original GC method provides, for these families of compounds, better results than the version proposed in 2004 by Zábanský and Růžička<sup>[2]</sup>, with relative deviations of 2.8% for the later and 3.2% for the former. For diols smaller deviations are observed for EG, within (0.9-1.2)%. It is worth noting that despite the deviations observed the GC method results, for the same compound, are coherent with the data of some authors<sup>[74,131,147,148]</sup>.

Other interesting fact, depicted in Figure 4.2.1, is the behavior of the heat capacities with temperature where a minimum in the relative deviations and a continuous loss of accuracy is observed with the increase of the temperature. This behavior denotes a limitation of the GC method in describing the effect of the temperature for this property.

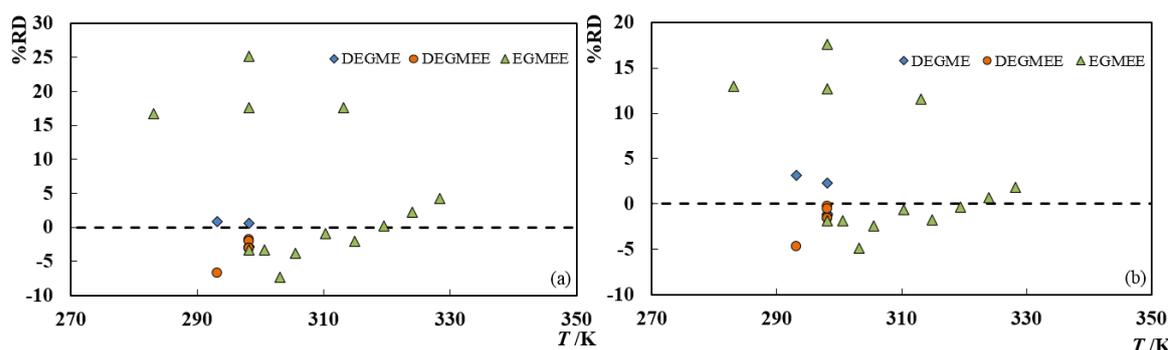


**Figure 4.2.1-** Relative deviations between heat capacity estimated by Zábanský and Růžička<sup>[2]</sup> (right figure); by Růžička and Domalski<sup>[1]</sup> (left figures) and the literature<sup>[37,38,109,111,147-154]</sup> as functions of temperature for: EG, DEG, TriEG and TetraEG a) and b); DEGME, TriEGDME, TetraEGDME, and DEGDEE c) and d).

TetraEGDME and DEGDEE c) and d)

For glymes and diethylene glycol diethyl ether, Figure 4.2.1c and Figure 4.2.1d, it can be observed a slight improvement of the heat capacities description when using the GC method amended by Zábbranský and Růžička<sup>[2]</sup>, where smaller average relative deviations of 0.30%, compared to 2.49% obtained from the original GC method, for the experimental data from Conesa et al.<sup>[109]</sup>, are observed. For triethylene glycol dimethyl ether even though the %AAD between the two methods evaluated are not significantly different the method proposed by Růžička and Domalski<sup>[1]</sup> overestimates the heat capacities while that proposed by Zábbranský and Růžička<sup>[2]</sup> underestimates it. Besides scarce, experimental data for tetraethylene glycol dimethyl ether is best described by the method proposed by Růžička and Domalski<sup>[1]</sup> with %AAD of 0.46%, %AAD lower than the other version for which 3.43% are observed.

Finally, for the last, group of glycols containing one hydroxyl group the method proposed by Zábbranský and Růžička<sup>[2]</sup> presents lower deviations. It can be also observed some discrepancies between authors for ethylene glycol monoethyl ether<sup>[116,155]</sup>.



**Figure 4.2.2-** Relative deviations between heat capacity estimated by Zábbranský and Růžička<sup>[2]</sup> (right figure); by Růžička and Domalski<sup>[1]</sup> (left figures) and the literature<sup>[35,36,39,40,150,155]</sup> as functions of temperature for: EGMEE, DEGME and DEGMEE a) and b);

As a form of conclusions the method from Zábbranský and Růžička<sup>[2]</sup> originally presented in 1993 is able to better predict heat capacity for glycols with one hydroxyl group, diethylene glycol and for diethylene dimethyl ether. By other hand, the remaining compounds are better described by the Růžička and Domalski<sup>[1]</sup> version. Nonetheless, it is notorious that both versions are able to predict the heat capacities of the compounds studied with deviations within the uncertainty of the deviations found among authors.

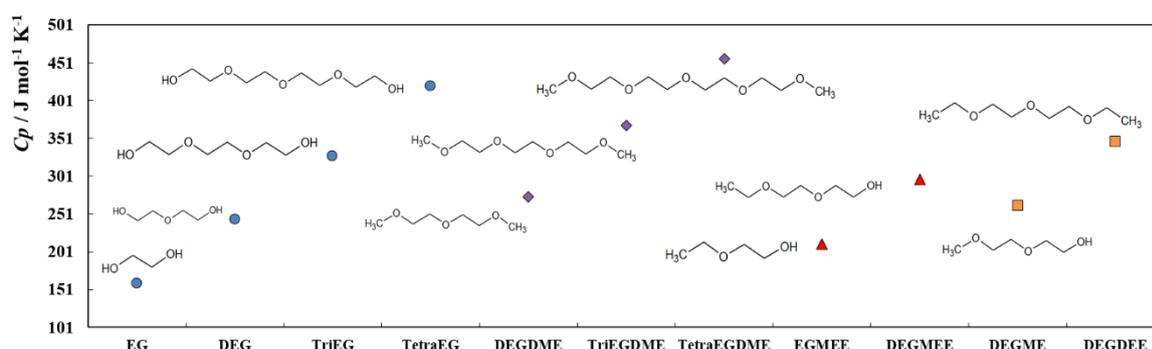
**Table 4.2.1-** %AAD for heat capacity within the range of temperature (270 - 350) K using the method proposed by Růžička and Domalski<sup>[1]</sup> and Zábbranský and Růžička<sup>[2]</sup>.

%AAD	EG	DEG	TriEG	TetraEG	DEGDME	DEGDDEE	TriEGDME	TetraEGDME	EGMEE	DEGMEE	DEGME
Růžička and Domalski <sup>[1]</sup>	0.918	4.109	2.610	3.029	2.662	2.227	1.622	0.462	8.038	3.330	1.980
Zábbranský and Růžička <sup>[2]</sup>	1.143	3.786	4.160	4.767	2.038	4.690	2.591	3.426	5.486	1.740	1.791

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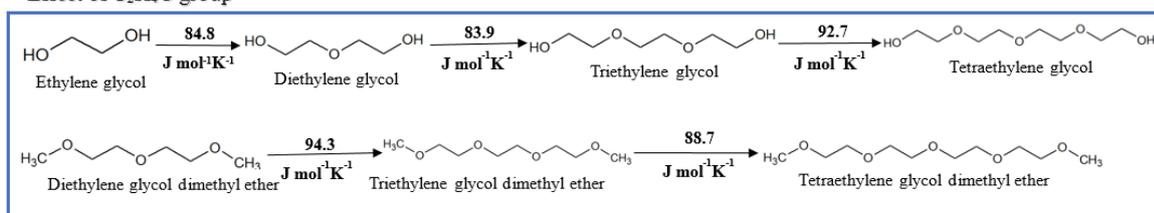
In fact, both group contribution method cannot be used on modelling purposes because they do not describe adequately the behaviour of experimental data with temperature. Nonetheless, the evaluation done before can help identifying the more reliable data sets, with the highest quality/accuracy. Thus, the data from Stephens et al.<sup>[147]</sup>, Svoboda et al.<sup>[155]</sup> and Conesa et al.<sup>[109]</sup> can be easily identified as that more accurate for ethylene glycol, ethylene glycol monoethyl ether and diethylene glycol dimethyl ether, respectively.

On the same manner as studied here with other properties, it was also looking into the impact of the molecular structures on heat capacity. For that, it was used the experimental data at 298.15 K according with the evaluation done with the group contribution method. On Figure 4.2.3, it shows the heat capacity as a function of the molecules.

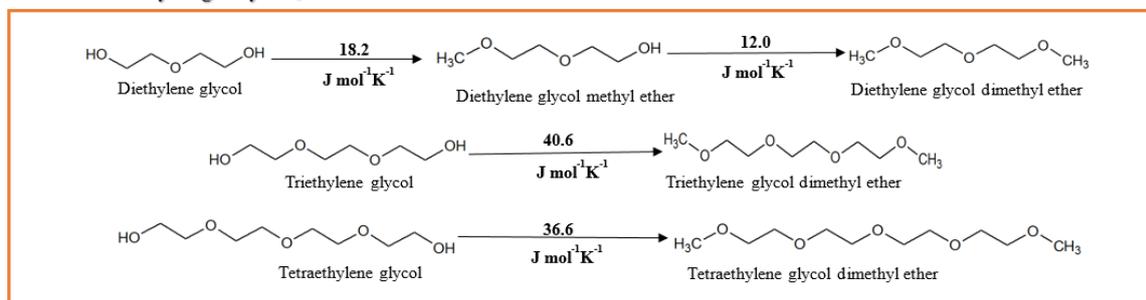


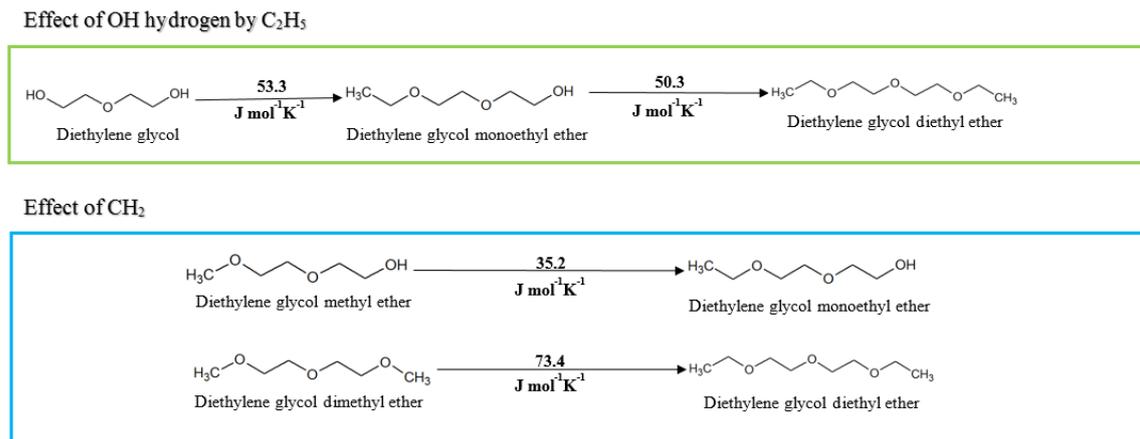
**Figure 4.2.3-** Heat capacity as a function of the compounds studied, at 293.15 K. Experimental data EG<sup>[147]</sup>, DEG<sup>[147]</sup>, TriEG<sup>[147]</sup>, TetraEG<sup>[147]</sup>, DEGDME<sup>[149]</sup>, TriEGDME<sup>[149]</sup>, TetraEGDME<sup>[38]</sup>, EGME<sup>[40]</sup>, DEGME<sup>[35]</sup>, DEGDEE<sup>[35]</sup>.

### Effect of C<sub>2</sub>H<sub>4</sub>O group



### Effect of OH hydrogen by CH<sub>3</sub>





**Figure 4.2.4-** Impact of the molecular structure on heat capacity at 298.15 K and atmospheric pressure.

As depicted in Figure 4.2.3 and it observes that glycols and glymes heat capacities increase with the number of the ethoxy groups (C<sub>2</sub>H<sub>5</sub>O). In fact, glycols heat capacity increment obtained are not regular, even experimental data are from the same authors Stephens et al.<sup>[147]</sup>.

The substitution of a hydrogen of one of the diols hydroxyl groups by a CH<sub>3</sub>, like on the pair DEG–DEGME, leads to a slight increase on the heat capacity, as presented in Figure 4.2.4. Moreover, even though the substitution of one hydrogen by a CH<sub>3</sub> groups leads to a significant increase on the heat capacity, the substitution of both terminal hydrogens, like on the pairs DEG–DEGDME, TriEG–TriEGDME and TetraEG–TetraEGDME, leads to a slightly higher increase to that observed to one substitution.

By the other hand, changing the hydrogen atom from the hydroxyl terminal group (-OH) by an ethyl group (-C<sub>2</sub>H<sub>5</sub>) leads to a higher increase on the heat capacity than that observed by adding a CH<sub>3</sub> group, like in the cases of DEG to DEGMEE and DEGMEE to DEGDEE (see Figure 4.2.4).

Nonetheless, adding more CH<sub>2</sub> in the molecules chain provides higher heat capacity increase, so more amount of energy is required to increase one kelvin for one mole of compounds, as expected. The amount of energy due to the adding of CH<sub>2</sub> is seem to be constant, as shown in Figure 4.2.4.

It is important to note, that some effect analysed not presents regular values on the property due to mainly of the source of these data are not from the same work and the same authors.

## 4. Results and Discussion

### 4.2.2. Extending Soft-SAFT EoS accuracy using heat capacity to enhance the molecular parameters determination

As discussed in Chapter 3, the molecular parameters determined and proposed as the best set, to describe the compounds vapour pressure and density, do not provide an accurate description of other properties for all the compounds. Furthermore, in this section it was also shown that the capacity of the molecular parameters proposed has a good prediction. In fact, soft-SAFT is not able to describe correctly the density of some glycol ethers and glymes, as discussed before. Furthermore, the association scheme adopted was the most suitable for the compounds here studied and therefore, no reason to doubt its consistency. Nonetheless, back in 2013, de Villiers et al.<sup>[56]</sup> stated that the use of more properties and pressure conditions, on top of density and vapour pressure at equilibrium condition, on the soft-SAFT molecular parameters fitting could provide more accurate molecular parameters that by their turn could assure a better performance of the EoS when used predictively. According to progressing studies<sup>[156]</sup> evidence shows that heat capacities could be the best approach to enhance the EoS molecular parameters estimation, overlapping the known deficiency of these type of EoS to describe derivative properties. Thus, aiming to improve soft-SAFT EoS performance new molecular parameters fitted not only to the vapour pressure and density but also to the heat capacities will be investigated.

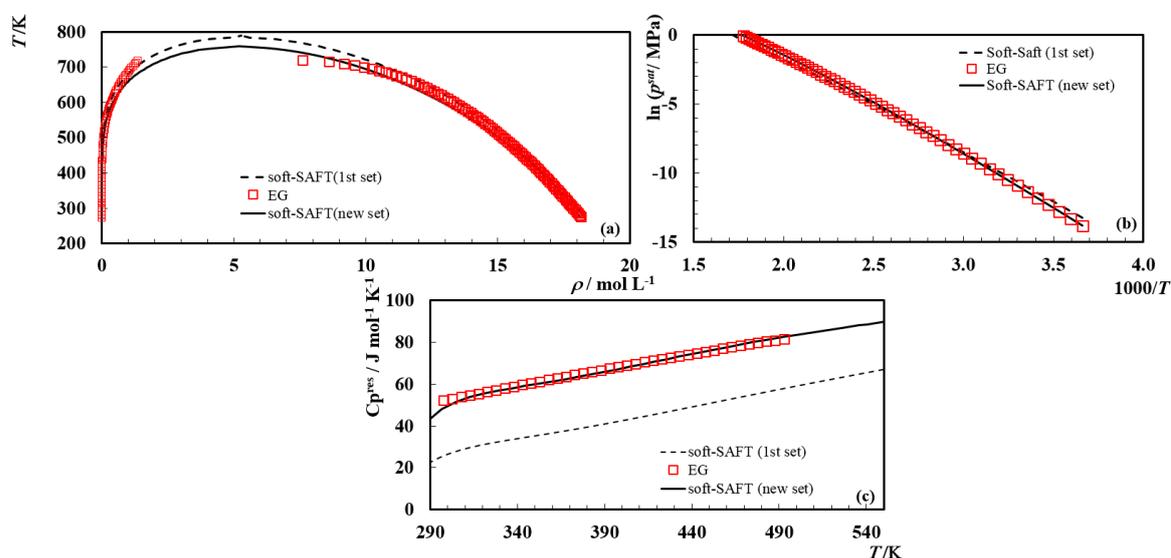
With that in mind and aiming to enhance soft-SAFT performance new molecular parameters were determined by fitting the EoS parameters against density, vapour pressure and heat capacities. Due to the lack of time and looking to, at least, test new molecular parameters for each of the compounds families studied, new molecular parameters were determined only for ethylene glycol, ethylene glycol monoethyl ether and diethylene glycol dimethyl ether. In addition, we also predict the heat capacity using the molecular parameter proposed in chapter 3, in order to see the ability of the new molecular parameters to improve the results.

For the fitting of the new molecular parameters, it was used the vapour pressure, density and heat capacity obtained by the correlations from DIPPR, as experimental data. It worth mentioning that the correlation of DIPPR to calculate the heat capacity for ethylene glycol, and ethylene glycol used the data from Stephens et al.<sup>[147]</sup>, and Svoboda et al.<sup>[155]</sup>, respectively for its regression. However, for diethylene glycol dimethyl ether it was used the experimental data from Conesa et al.<sup>[109]</sup>. With that in mind, after optimizing the best set of molecular parameters by soft-SAFT, the new set of molecular parameters for the three compounds are reported in Table 4.2.2.

**Table 4.2.2-** Molecular parameters proposed by fitting density, vapour pressure and residual heat capacity.

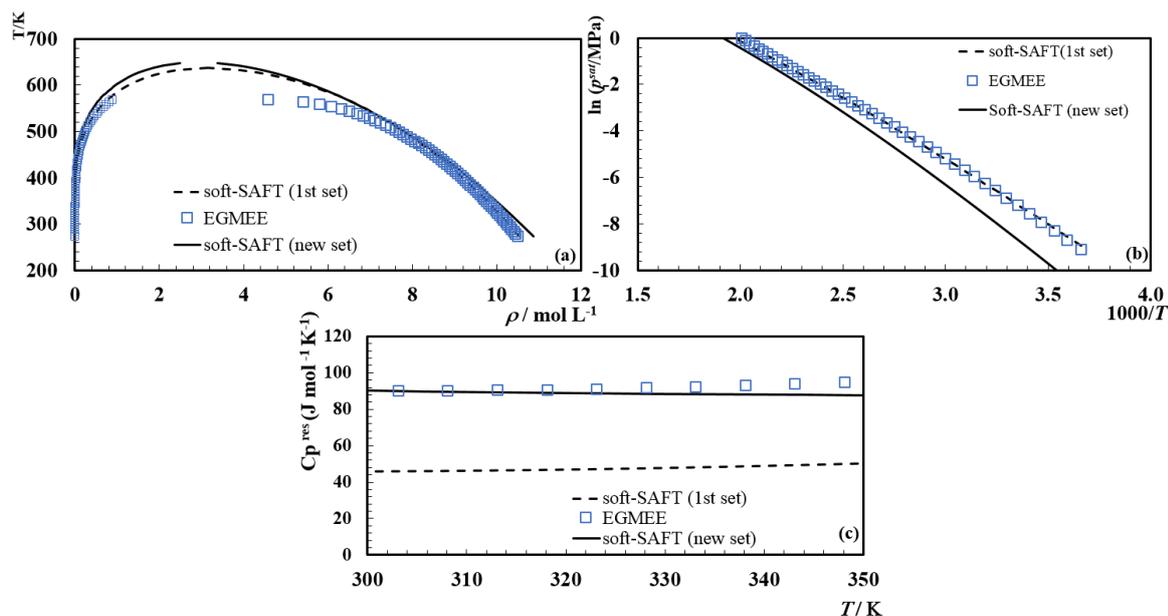
Compound	T/K		Molecular parameters					%AAD			T/K	
	Tmin	Tmax	m	$\sigma$ (Å)	$\varepsilon/k_B$ (K)	$\varepsilon^{HB}/k_B$ (K)	$k_{HB}$ (Å)	r	$p^{sat}$	$C_p^{res}$	Tmin	Tmax
Ethylene glycol	328.15	508.15	2.534	3.227	330.51	3520.65	2705.42	0.301	0.301	0.926	328.15	493.15
Diethylene glycol dimethyl ether	308.15	393.15	5.328	3.288	242.55			0.441	4.439	6.003	312.56	421.45
Ethylene glycol monoethyl ether	283.15	463.15	3.182	2.268	266.67	2429.23	2383.81	1.329	5.382	3.213	303.15	348.15

For ethylene glycol the new molecular parameters, reported in Table 4.2.2, allow not only a better description of the compounds densities and vapour pressures, as shown in Figure 4.2.5, but also a better description of the heat capacities, with a %AAD of 0.96%. In fact, the %AAD obtained in the entire range of temperatures (273.15 to  $T_c$ ) for the density (1.8%) and vapour pressure (14.4%) are lower than those reported in Table 3.1.5 with the first set of molecular parameters proposed for this compound.



**Figure 4.2.5-** Molar density (a), logarithmic of vapour pressure (b) and residual heat capacities (c) as function of temperature for the ethylene glycol. The dashed and solid lines represent the soft-SAFT EoS using the first and new set molecular parameter, respectively.

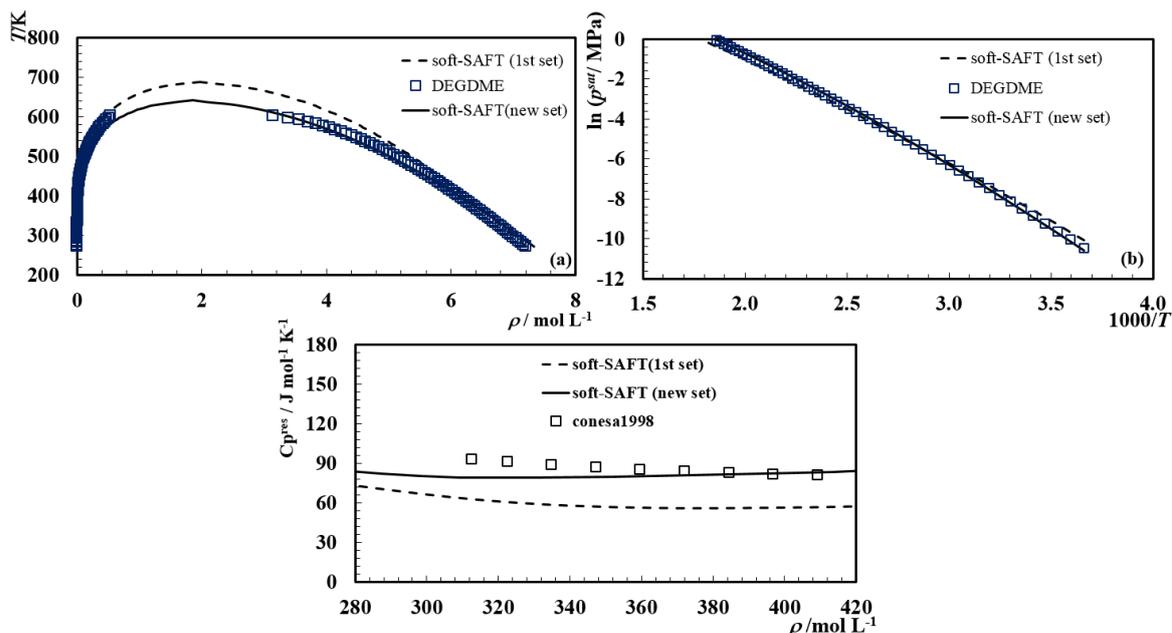
## 4. Results and Discussion



**Figure 4.2.6-** Molar density (a) logarithmic of vapour pressure (b) and residual heat capacities (c) as function of the temperature for ethylene glycol monoethyl ether. The dashed lines and solid lines represent the soft-SAFT EoS using the first and new set of molecular parameters, respectively.

For ethylene glycol monoethyl ether, the results show that even though soft-SAFT EoS description of the heat capacities is improved, a loss on the EoS description for the density and vapour pressure is evident, as depicted in Figure 4.2.6, and the calculated %AADs are 3.9% and 47.1%, respectively.

For diethylene glycol dimethyl ether, the new molecular parameters enhance soft-SAFT description both for density and vapour pressure, and also the heat capacity, as it can be demonstrated in Figure 4.2.7. It can also be proved with the lower deviations for the density and the vapour pressure, which are 1.4% and 5.0% respectively in the interval range of temperature (273.15-608.15) K.



**Figure 4.2.7-** Molar density (a) logarithm of vapour pressure (b) and liquid residual heat capacities (c) as a function of the temperature for diethylene glycol dimethyl ether. The dashed lines and solid lines represent the soft-SAFT EoS using the first and new set of molecular parameters, respectively.

Based on these results, one can corroborate the hypothesis presented by de Villers et al.<sup>[56]</sup> and Oliveira et al.<sup>[156]</sup>, that the use of larger set of properties, temperatures and pressure, will enhance soft-SAFT molecular parameters optimization. In fact, adding the residual heat capacity to the fitting methodology improves the descriptions of all the properties evaluated. In fact, the use of this methodology should be implemented in future soft-SAFT applications.

#### 4.2.3. Viscosity

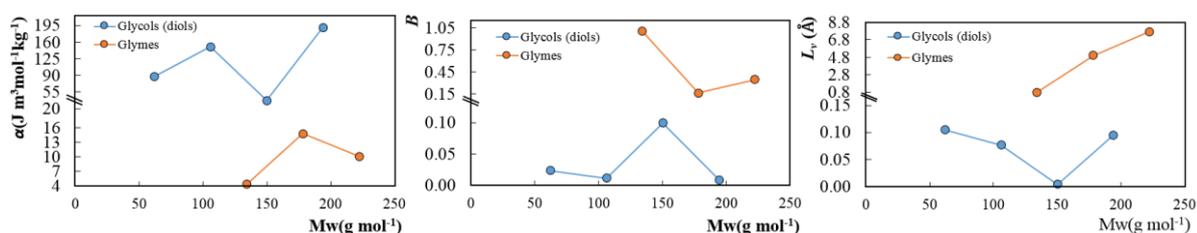
To determine the viscosity by soft-SAFT, we used our experimental data which are reported in section 4.1.3 and the molecular parameters proposed in chapter 3. Three new parameters, namely,  $\alpha$  ( $\text{J m}^3/(\text{mol kg})$ ) which describes the proportionality between the energy barrier and the density,  $B$  that corresponds to the free volume overlap and  $L_v$  ( $\text{\AA}$ ) that is the length parameter related to the structure of the molecules and the characteristic relaxation time were fitted to the experimental data. These new parameters are reported Table 4.2.3.

As already presented in Figure 4.1.15 on section 4.1.3, the results show that the model here used (soft-SAFT coupling with the FVT) provides a good description of the viscosity experimental data. It was observed some limitations at the lower temperature where the model FVT underestimates the viscosity for some compounds.

## 4. Results and Discussion

**Table 4.2.3** soft-SAFT viscosity molecular parameters and %AAD between soft-SAFT and the experimental viscosity for the studied compounds.

Compound	$\alpha$ (J m <sup>3</sup> /(mol kg))	$B$	$L_v$ (Å)	%AAD
Ethylene glycol	88.01	0.02335	0.1042	2.87
Diethylene glycol	150.4	0.01133	0.07637	3.88
Triethylene glycol	37.14	0.09972	0.003740	4.41
Tetraethylene glycol	190.7	0.008295	0.09466	4.46
Diethylene glycol dimethyl ether	4.332	1.006	0.8144	0.816
Diethylene glycol diethyl ether	29.55	0.05665	2.447	0.276
Triethylene glycol dimethyl ether	14.74	0.1634	4.999	1.03
Tetraethylene glycol dimethyl ether	10.06	0.3482	7.745	1.83
Ethylene glycol monoethyl ether	27.68	0.08005	1.394	0.855
Diethylene glycol methyl ether	8.714	0.4480	5.200	1.82
Diethylene glycol monoethyl ether	7.545	0.6362	5.892	2.19



**Figure 4.2.8-** Viscosity parameter as functions of molecular weights for glycols (diols) and glymes.

As shown in Figure 4.1.15, soft-SAFT with the FVT is able to describe the viscosity of all the glycols studied and no degradation is observed for the glymes as in the case of density.

An analysis was also made for the trends of the viscosity parameters, as it was done for the molecular parameters ( $m$ ,  $\sigma$ ,  $\epsilon^{HB}/k_B$ ). It was not possible to establish a correlation between the molecular weight of the compounds and the new molecular parameters values, as depicted in Figure 4.2.8. The only exception is the parameter  $L_v$  that presents a linear tendency with the glymes' molecular weight.

Since in **section 4.2.2** it was also proposed a new set of molecular parameters, it was used on the fitting of the new set of required parameters for the viscosity. As expected, the results are also good, as shown by their low deviation between our data and soft-SAFT results. A slight bigger deviation was obtained using the new set of parameters than those obtained in Table 4.2.3.

**Table 4.2.4-** New parameters for determining the viscosity using the new set of molecular parameters proposed.

Compound	$\alpha$ (J m <sup>3</sup> /(mol kg))	$B$	$L_v$ (Å)	%AAD
Ethylene glycol	75.89	0.02725	0.1847	3.18
Diethylene glycol dimethyl ether	2.197	2.582	0.8257	0.949
Ethylene glycol monoethyl ether	1.783	4.300	25.99	0.926

It is important to mention that these viscosity parameters are obtained by the fitting of

#### *4. Results and Discussion*

experimental viscosity data supplied in this work and using the molecular parameters proposed in order to predict the molar density required in the model of FVT. Since the experimental data for the viscosity data reported here are in good agreement and present low deviations with other authors in the literature. It can be argued that the three viscosity parameters in Table 4.2.3 and Table 4.2.4 can be used in other equations of state to estimate the viscosity of glycols, glymes or glycol ethers studied without needed experimental data, coupling the FVT model.



## 5. Conclusions



In order to overcome the demand for reliable and accurate data, this thesis reports new experimental thermophysical data for 11 pure glycols, for density, viscosity and refractive index within the temperature range (288.15 – 373.15) K at atmospheric pressure. There is no significant or systematic deviations between the data measured here and those reported in the literature

Furthermore, and besides characterizing the set of selected glycols this work was able to study the behaviour of the molecules in each property measured. With that, it was observed that the glycols density, viscosity and refractive index increase with the increasing of the molecular chain of glycols, as observed for other organic compounds. The only exception was for diethylene glycol diethyl ether that presents lower deviations than all remaining compounds, and in terms of molar volume, it stands for the highest molar volume. Another exception was also diethylene glycol methyl ether that despite having a CH<sub>2</sub> group less than the diethylene glycol monethyl ether, presents higher densities. This fact is due to the additive molar volume of (CH<sub>2</sub>) group. On the basis of this observation, it can conclude that the former has a more organized and compact bulk. Besides this effect, it was also shown that the impact of replacing the hydrogen(s) of the glycols hydroxyl group by a methyl (CH<sub>3</sub>) or an ethyl (C<sub>2</sub>H<sub>5</sub>) leads to a significant decrease of the property values (density, refractive index and viscosity). But the effect of changing the hydroxyl group hydrogen by an ethyl group rather than by a methyl has a greater impact on the density, than on the viscosity and refractive indices.

Due to the importance of reliable models to be used in process simulation, the soft-SAFT EoS was extended to describe and predict thermophysical properties of glycols. Hence, it was here tested the associative scheme proposed by Pedrosa et al.<sup>[8]</sup> for describing the behaviour of pure glycols (EG, DEG, triEG and tetraEG) proposing new molecular parameters without fixing the association parameters. Since our results have lower deviations for the density and vapour pressure than those obtained using the molecular parameters from Pedrosa and co-workers for glycols, hence, new molecular parameters for the others glycols, applying the same associative scheme, were also attempted for the first time, but the results show that glycols are not correctly described for temperatures above 400 K. For that reason, other associative schemes were evaluated, in order to increase the accuracy with increasing of the temperature, nonetheless, no significant improvement was obtained. In this way the molecular parameters initially proposed were used for the rest of the work. Furthermore, it was also predicted the heat capacity by soft-SAFT for some glycols and the results shown not good agreement with

## 5. Conclusions

the experimental data.

A group contribution method was used to perform a critical analysis of the quality of available heat capacity for glycols. It was possible to identify the sets of experimental data more reliable and with the highest quality for further modelling proposes. Since with the molecular parameters proposed, it was found some discrepancies and loss of accuracy with temperature mainly for glymes and some deviation on the prediction of other properties, new soft-SAFT molecular parameters were determined by using heat capacities together with density (liquid and vapour phase) and vapour pressures. Our results support and reinforce the idea that using heat capacities, along with density (liquid and vapour phase) and vapour pressures assures a better description for the compounds evaluated.

## 6. Future work



Since this work was very challenging due to the combination of experimental and modelling studies, we recommend to apply the new approach using the heat capacity in the soft-SAFT parameterization for the fitting of the remaining glycols studied here.

To complete this work, it will also be interesting to check the ability of the new molecular parameters proposed here in the prediction of others thermodynamics properties such as: speed of sound, surface tension and others thermodynamics properties.

Afterwards, we suggest to measure high pressure density of glycols and evaluate the impact of using them on the molecular optimizations methodology.

In addition, we also recommend that after optimized new molecular parameter with the new methodology, to adjust new parameters of the viscosity model to evaluate some tendency of these parameters with the molecular weights.



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# Appendix

## Appendix A- Experimental measurements

**Table A.1-** Experimental density for the compounds studied at atmospheric pressure.

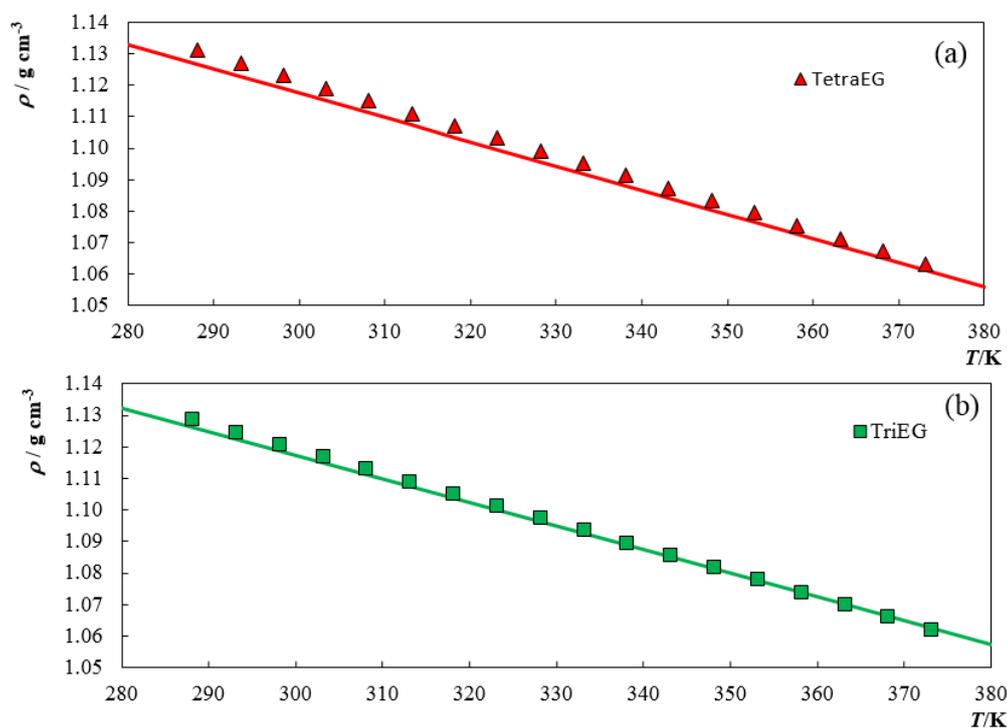
$T \pm 0.02$ K	EG	DEG	TriEG	TetraEG	DEGDME	DEGDDEE	TriEGDME	TetraEGDME	EGMEE	DEGME	DEGMEE
	$\rho \pm 0.0005$ g.cm <sup>-3</sup>										
288.15	1.1182	1.1214	1.1286	1.1312	0.9502	0.9144	0.9908	1.0170	0.9368	1.0253	0.9939
293.15	1.1146	1.1178	1.1246	1.1271	0.9452	0.9096	0.9860	1.0123	0.9323	1.0210	0.9894
298.15	1.1111	1.1142	1.1207	1.1231	0.9402	0.9047	0.9815	1.0076	0.9277	1.0163	0.9849
303.15	1.1076	1.1106	1.1168	1.1191	0.9352	0.8998	0.9767	1.0031	0.9231	1.0119	0.9804
308.15	1.1041	1.1070	1.1129	1.1151	0.9302	0.8950	0.9719	0.9988	0.9185	1.0074	0.9760
313.15	1.1005	1.1034	1.1090	1.1111	0.9252	0.8901	0.9672	0.9941	0.9139	1.0030	0.9715
318.15	1.0970	1.0997	1.1051	1.1072	0.9202	0.8853	0.9624	0.9895	0.9093	0.9988	0.9670
323.15	1.0934	1.0961	1.1012	1.1032	0.9152	0.8804	0.9577	0.9849	0.9046	0.9943	0.9625
328.15	1.0898	1.0925	1.0973	1.0992	0.9101	0.8756	0.9529	0.9802	0.8999	0.9898	0.9581
333.15	1.0862	1.0888	1.0934	1.0953	0.9050	0.8707	0.9481	0.9756	0.8951	0.9853	0.9535
338.15	1.0826	1.0852	1.0895	1.0913	0.8999	0.8659	0.9433	0.9710	0.8904	0.9810	0.9490
343.15	1.0789	1.0815	1.0856	1.0873	0.8948	0.8610	0.9386	0.9665	0.8855	0.9765	0.9444
348.15	1.0752	1.0778	1.0817	1.0834	0.8897	0.8561	0.9338	0.9619	0.8807	0.9718	0.9399
353.15	1.0715	1.0741	1.0778	1.0794	0.8846	0.8512	0.9290	0.9573	0.8758	0.9672	0.9353
358.15	1.0678	1.0703	1.0738	1.0753	0.8794	0.8463	0.9242	0.9527	0.8710	0.9625	0.9307
363.15	1.0640	1.0666	1.0698	1.0713	0.8742	0.8414	0.9194	0.9481	0.8661	0.9579	0.9261
368.15	1.0602	1.0628	1.0659	1.0673	0.8690	0.8365	0.9145	0.9435	0.8612	0.9531	0.9214
373.15	1.0564	1.0590	1.0619	1.0632	0.8638	0.8316	0.9097	0.9389	0.8563	0.9485	0.9168

**Table A.2-** Experimental refractive indices for the compounds studied at atmospheric pressure.

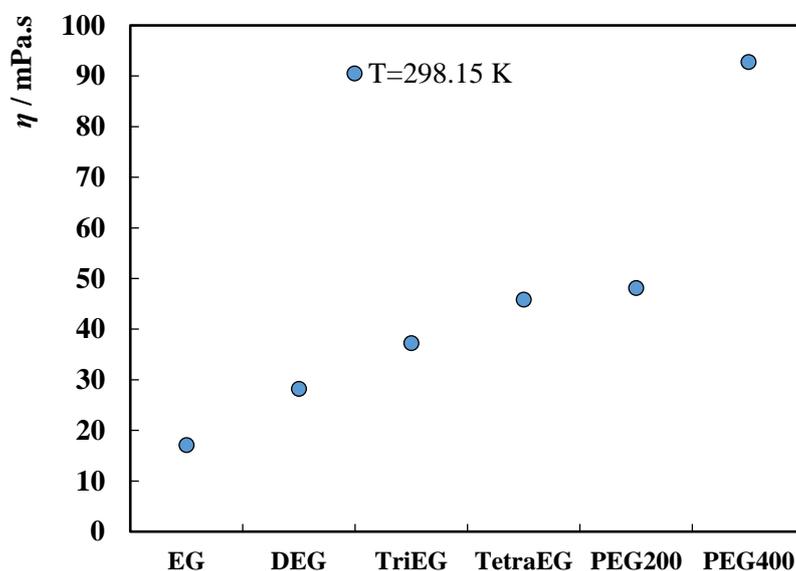
$T \pm 0.05$ °C	$n \pm 2 \times 10^{-5} \eta_D$										
	EG	DEG	TriEG	TetraEG	DEGDME	DEGDDEE	TriEGDME	TetraEGDME	EGMEE	DEGME	DEGMEE
10.00	1.434613	1.450192	1.459436	1.463326	1.412491	1.416579	1.427122	1.435990	1.416444	1.429141	1.431100
15.00	1.433116	1.448597	1.457741	1.461690	1.410200	1.414280	1.424981	1.434141	1.411922	1.427232	1.429160
20.00	1.431665	1.447015	1.456099	1.459994	1.408017	1.412024	1.422837	1.431955	1.410235	1.424977	1.427113
25.00	1.430000	1.445398	1.454467	1.458273	1.405790	1.409775	1.420705	1.429922	1.408029	1.423900	1.425005
30.00	1.428551	1.443762	1.452833	1.456609	1.403592	1.407485	1.418622	1.427771	1.406132	1.421735	1.422895
40.00	1.425615	1.440675	1.449552	1.453190	1.399205	1.402964	1.414338	1.423725	1.401800	1.417332	1.418869
50.00	1.422599	1.437449	1.446257	1.449762	1.394899	1.398380	1.410050	1.419731	1.396910	1.413679	1.414830
60.00	1.419552	1.434238	1.442927	1.446331	1.390501	1.393816	1.405788	1.415783	1.392711	1.410097	1.410820
70.00	1.416547	1.431049	1.439556	1.442877	1.386228	1.389286	1.401533	1.411735	1.388485	1.406350	1.406833
80.00	1.413508	1.427861	1.436222	1.439471	1.381778	1.384737	1.397233	1.407726	1.384300	1.402411	1.402759

**Table A.3-** Experimental viscosity for the glycols at atmospheric pressure.

$T \pm 0.02$ K	$\eta \pm 0.35\%$ mPa.s										
	EG	DEG	TriEG	TetraEG	DEGDME	DEGDDEE	TriEGDME	TetraEG	EGMEE	DEGME	DEGMEE
288.15	26.8010	47.1420	63.5660	79.7100	1.1607	1.4830	2.4135	4.3366	2.3138	4.5144	5.1570
293.15	21.1970	36.0200	48.0470	59.6780	1.0809	1.3630 <sup>a</sup>	2.1621	3.8457	2.0663	3.9630	4.4658
298.15	17.1340	28.2330	37.2700	45.8620	1.0108	1.2541	1.9562	3.3348	1.8447	3.4032	3.8106
303.15	13.9980	22.4780	29.4130	35.9230	0.9423	1.1557	1.7773	2.9666	1.6610	3.0001	3.3284
308.15	11.5770	18.1800	23.5990	28.6460	0.8786	1.0671	1.6232	2.6595	1.5028	2.6656	2.9326
313.15	9.6266	14.8520	19.1580	23.1580	0.8251	0.9874	1.4389	2.3893	1.3648	2.3726	2.5921
318.15	8.1815	12.3930	15.8630	19.0800	0.7668	0.9160	1.3727	2.1826	1.2473	2.1484	2.3308
323.15	6.9798	10.4180	13.2520	15.8870	0.7182	0.8522	1.2698	1.9948	1.1427	1.9461	2.0993
328.15	6.0067	8.8494	11.1920	13.3800	0.6742	0.7952	1.1788	1.8319	1.0505	1.7721	1.9011
333.15	5.1971	7.5702	9.5277	11.3670	0.6332	0.7443	1.0635	1.6774	0.9621	1.6062	1.7178
338.15	4.5554	6.5612	8.2213	9.7840	0.5986	0.6987	1.0264	1.5659	0.8948	1.4885	1.5830
343.15	4.0096	5.7178	7.1372	8.4795	0.5662	0.6578	0.9616	1.4560	0.8288	1.3718	1.4556
348.15	3.5519	5.0192	6.2432	7.4052	0.5369	0.6209	0.9032	1.3579	0.7698	1.2683	1.3430
353.15	3.1609	4.4294	5.4865	6.4912	0.5051	0.5871	0.8143	1.2503	0.7245	1.1552	1.2251
358.15	2.8348	3.9444	4.8743	5.7623	0.4862	0.5559	0.8013	1.1882	0.6659	1.0936	1.1534
363.15	2.5519	3.5269	4.3461	5.1267	0.4640	0.5263	0.7563	1.1153	0.6227	1.0192	1.0715
368.15	2.3062	3.1693	3.8959	4.5846	0.4444	0.4978	0.7153	1.0473	0.5835	0.9502	0.9972
373.15	2.1019	2.8714	3.5154	4.1157	0.4410	0.4696	0.6499	0.9781	0.5181	0.8767	0.9208



**Figure A.1-** Density as function of temperature of the studied TetraEG (a) and TriEG(b). The solid lines represent the soft-SAFT EoS.



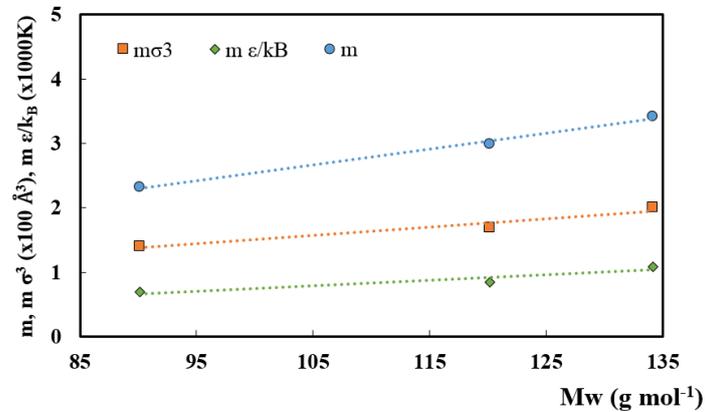
**Figure A.2-** The number of ethoxy group effect in glycols, glymes, PEG200<sup>[120]</sup> and PEG400<sup>[120,121]</sup> on the refractive index at 298.15 K.

## Appendix B- Thermodynamics' constants

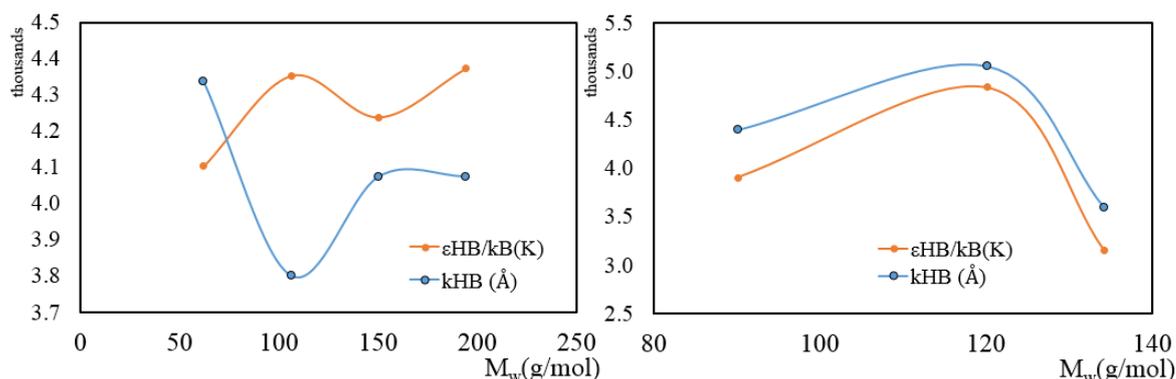
**Table B 1-** Thermodynamics Properties used in the calculation in this thesis from<sup>[74]</sup>

Chemical	CAS.Num	Mw(g/mol)	Chemical fomulas	T <sub>melt</sub> /K	T <sub>boil</sub> /K	T <sub>C</sub> /K	P <sub>c</sub> /Pa	V <sub>c</sub> (m <sup>3</sup> /kmol)	ω
Ethylene Glycol	107-21-1	62.068	C2H6O2	260.15	470.45	720	8.20E+06	0.191	0.50678
Diethylene Glycol	111-46-6	106.122	C4H10O3	262.7	517.96	744.6	4.60E+06	0.312	0.62211
Triethylene glycol	112-27-6	150.175	C6H14O4	265.95	561.5	769.5	3.32E+06	0.443	0.75595
Tetraethylene glycol	112-60-7	194.228	C8H10O5	268.15	602.7	795	2.59E+06	0.564	0.91744
Diethylene glycol dimethyl ether	112-36-7	134.175	C6H14O3	209.11	435.65	608	2.86E+06	0.422	0.5775
Diethylene glycol diethyl ether	111-96-6	162.229	C8H18O3	228.85	462.15	624	2.37E+06	0.558	0.68067
Triethylene glycol dimethyl ether	112-49-2	178.229	C8H18O4	229.35	486.15	651	2.31E+06	0.548	0.79153
Tetraethylene glycol dimethyl ether	143-24-8	222.282	C10H22O5	243.45	548.95	705	1.94E+06	0.674	0.9652
Ethylene glycol monoethyl ether	110-80-5	90.112	C4H10O2	214.15	408.15	569	4.24E+06	0.294	0.75818
Diethylene glycol monoethyl ether	111-90-0	134.175	C6H14O3	219.15	476.06	656	3.14E+06	0.436	0.68076
Diethylene glycol methyl ether	111-77-3	120.148	C5H12O3	208.15	466.15	630	3.54E+06	0.367	0.87074

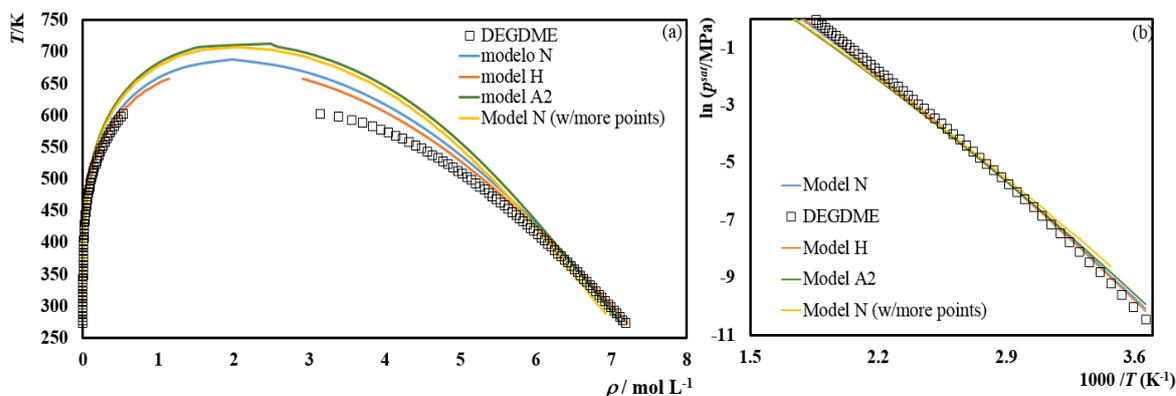
## Appendix C- Molecular parameter obtained for other association model



**Figure C. 1-** Molecular parameters for others association model soft-SAFT  $m$ ,  $\sigma$  and  $\epsilon/k_B$  molecular parameter as function of: ethylene glycol monoethyl ether and diethylene glycol methyl and ethyl ether molecular weight.



**Figure C.2-** soft-SAFT and  $\epsilon^{\text{HB}}/k_B$  and  $k^{\text{HB}}$  association molecular parameter as function of: a) ethylene glycol, di, tri and tetraethylene glycol; b) ethylene glycol monoethyl ether and diethylene glycol methyl and ethyl ether molecular weight

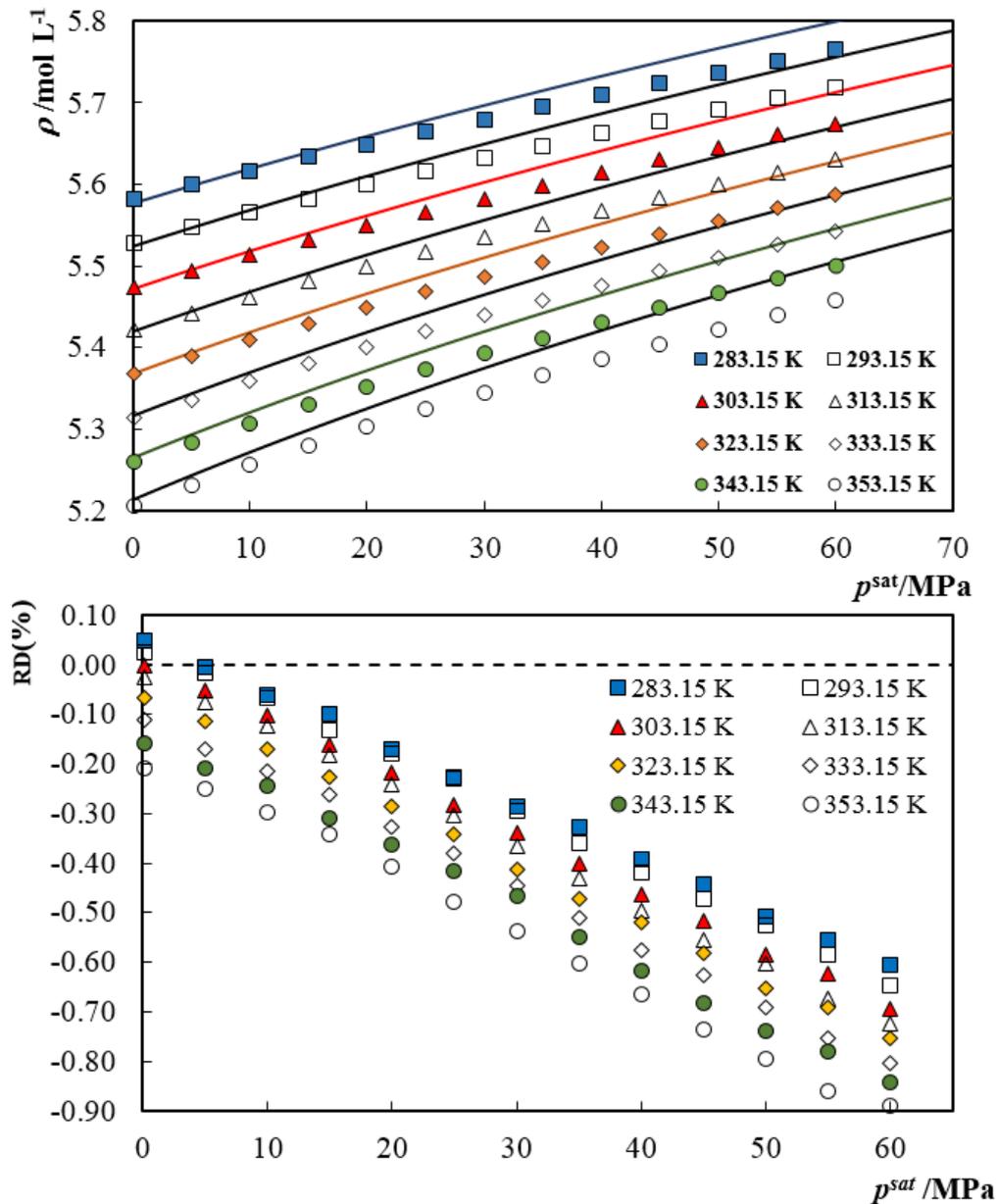


**Figure C.3-** Density of the vapour and liquid phase as function of temperature for diethylene glycol dimethyl ether. The solid lines correspond to the soft-SAFT results with the three different association model.

**Table C.1-** soft-SAFT molecular parameters for other association model used, temperature range of the experimental data used for the parameters fit and %AAD between the experimental and calculated density and vapour pressure data, for the studied compounds.

Compound	model	T/K		Molecular parameters					%AAD	
		$T_{\min}$	$T_{\max}$	$m$	$\sigma$ (Å)	$\epsilon/k_B$ (K)	$\epsilon^{\text{HB}}/k_B$ (K)	$k^{\text{HB}}$ (Å)	$\rho$	$p$
Ethylene glycol	AB	328.15	373.15	1.888	3.561	176.84	3408.3	34595.8	1.26	0.09
Diethylene glycol		328.15	373.15	4.597	2.933	139.73	3938.4	2661.5	0.40	0.99
Triethylene glycol		348.15	373.15	6.348	2.873	4161.63	3685.9	3685.9	0.55	0.83
Tetraethylene glycol		358.15	373.15	10.343	2.455	107.66	4708.8	3777.2	0.43	0.84
Diethylene glycol dimethyl ether	A2	328.15	373.15	2.528	4.377	353.61	2070.5	2699.6	0.07	3.77
	H	328.15	373.15	3.699	3.780	290.59			2.66	0.05
		328.15	448.15	2.623	4.324	346.56			1.01	13.53
Ethylene glycol monoethyl ether	H	318.15	373.15	2.589	3.780	337.42			0.02	6.44
Diethylene glycol methyl ether		288.15	373.15	3.521	3.655	330.44			0.20	7.97
Diethylene glycol monoethyl ether		318.15	373.15	3.737	3.748	322.71			0.13	3.48

## Appendix D- Prediction of high pressure density by soft-SAFT



**Figure D.1-** Experimental high density pressure as function of pressure at different temperature versus the density predicted by soft-SAFT for TriEGDME (a) and relative deviation between experimental data and soft-SAFT prediction as function of pressure (b)

