



Isobaric vapor-liquid equilibrium of water + glymes binary mixtures: Experimental measurements and molecular thermodynamic modelling

Emanuel A. Crespo^a, Naima Chouireb^b, O. Tafat Igoudjilene^b, Lourdes F. Vega^c, Pedro J. Carvalho^{a,*}, João A.P. Coutinho^a

^a CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193, Aveiro, Portugal

^b Laboratory of Thermodynamic and Molecular Modeling, Faculty of Chemistry, USTHB, BP 32, El-Alia, Bab-Ezzouar, Algies, Algeria

^c Research and Innovation Center on CO₂ and H₂ (RICH), Catalysis and Separation Center (CeCaS) and Chemical Engineering Department, Khalifa University, PO Box 127788, Abu Dhabi, United Arab Emirates

ARTICLE INFO

Article history:

Received 6 December 2019

Received in revised form

5 February 2020

Accepted 27 February 2020

Available online 3 March 2020

Keywords:

Glymes

Water

Vapor-liquid equilibrium

Soft-SAFT

Activity coefficients

ABSTRACT

In this work, new experimental data on the isobaric vapor-liquid equilibria (VLE) of binary aqueous systems, with six different glycol ethers (glymes), some of which are currently used in the Selexol process, were measured at three different pressures, namely 0.05, 0.07, and 0.1 MPa.

From the experimental data, the water activity coefficients were estimated using the modified Raoult's law and used to infer about the effect of the glymes structure on their interactions with water. Moreover, using a coarse-grain molecular model previously proposed in the framework of the soft-SAFT equation of state (EoS) for both glycols and glymes, the experimental data were successfully correlated with a single state-independent binary interaction parameter and average absolute deviations from the experimental data of 1.30 K. Furthermore, the model was used in a predictive manner to obtain the water activity coefficients in the whole composition range, providing useful insights into the systems non-ideality.

© 2020 Elsevier B.V. All rights reserved.

1. Introduction

Regardless of its source, raw natural gas is significantly different from end-use natural gas, which is almost pure methane (CH₄). Instead, natural gas is a mixture of methane with different hydrocarbons such as ethane, propane, butane, i-butane, and a fraction of C₅₊, along with a number of impurities such as water, hydrogen sulfide (H₂S), mercaptans, carbon dioxide (CO₂) and nitrogen (N₂), among others. Consequently, the natural gas stream must be processed to remove the undesired hydrocarbons and impurities in order to meet the necessary specifications for pipeline transportation and final use. This purification process involves different sequential stages, starting with the removal of oil and condensates, dehydration/water removal, the separation of natural gas liquids, and finally the sweetening of the gas through the removal of sulfur-containing compounds, and acid gases such as H₂S and CO₂ whose presence in the final product is highly undesirable, to avoid the

formation of sulfuric and carbonic acid (highly corrosive to the equipment and pipelines) [1].

Glymes, or glycol ethers, are known by their affinity towards CO₂ and H₂S due to the presence of ethylene oxide groups that interact favorably with these compounds. Consequently, several authors reported large solubilities of these gases in glymes and their blends, showing them to be suitable solvents for gas sweetening applications [2–10]. Hence, the state-of-the-art process for gas sweetening at high pressures, the Selexol process by Honeywell UOP® [11], uses a mixture of different polyethylene glycol dimethyl ethers as a solvent that, in addition to dissolving large amounts of acid gases, presents several other desirable properties such as a low vapor pressure, low corrosion rates and easy regeneration [12].

Given the possible occurrence of residual water in the natural gas stream entering the Selexol process, where the water content can be further reduced increasing the performance of the process, a reliable knowledge of the phase behavior and interactions exhibited by aqueous glycol ether systems is required. In addition to helping in the CO₂ removal process already mentioned, this knowledge will also be applicable to a variety of other systems, as

* Corresponding author.

E-mail address: quijorge@ua.pt (P.J. Carvalho).

glycol ethers are often found in several personal, household, and industrial products containing water such as water-based paints, dyes, sunscreens, cosmetics, pharmaceuticals, etc [13].

Surprisingly, experimental data concerning the vapor-liquid equilibrium (VLE) of glycol ethers + water binary mixtures is scarce in the literature with experimental data being reported mainly for the smaller glycol ethers such as 2-methoxyethanol or 2-ethoxyethanol but not for the heavier polyethylene glycol dimethyl ethers such as those used in the Selexol process (e.g. triethylene glycol and tetraethylene glycol dimethyl ethers) [14]. Therefore, in this work, new experimental data on the isobaric VLE of binary systems composed of water and six different glycol ethers, namely ethylene glycol ethyl ether (EGEE), diethylene glycol methyl ether (DEGME), diethylene glycol ethyl ether (DEGEE), diethylene glycol dimethyl ether (DEGDME), triethylene glycol dimethyl ether (TriEGDME), and tetraethylene glycol dimethyl ether (TeEGDME), at three different pressures, are reported.

Moreover, recognizing the importance of accurate thermodynamic models for the development and optimization of new and existing industrial units, we have used a molecular model for polyethers, in the framework of soft-SAFT [15], an advanced equation of state (EoS), previously proposed and validated by some of us [16,17]. This model has also been used to successfully describe different types of experimental data including the CO₂ solubilities in glycol ethers [10] and the VLE of glycol + water binary mixtures [18]. Accordingly, in this work, the same model is used to correlate the newly reported experimental data, extending its proven versatility while providing further information regarding the magnitude of the interactions present in the system.

2. Experimental section

2.1. Materials

Vapor-liquid equilibria was measured for six glymes, namely, EGEE, DEGME, DEGEE, DEGDME, TriEGDME and TeEGDME at 0.05, 0.07, and 0.1 MPa.

Samples of each glycol ether were dried using 3 Å molecular sieves to remove traces of water. The water content was then determined using a Metrohm 831 Karl Fischer coulometer (using the Hydranal-Coulomat AG from Riedel-de Haëns as analyte). The water used to prepare the binary mixtures was double distilled and deionized, passed through a reverse osmosis process and then treated using a Milli-Q plus 185 water purification equipment. ¹H and ¹³C NMR were used to determine the compounds purity.

The name, chemical structure, molar mass, water content, purity and supplier of each glycol ether are reported in Table 1.

2.2. VLE measurements

The boiling temperatures of the binary systems under investigation were measured at (0.1, 0.07, and 0.05 MPa) using an in-house isobaric microebullimeter. The apparatus was previously optimized and validated, and its fully detailed description, including uncertainties, can be found in previous publications [19–21].

Essentially, the apparatus is composed by three sections: (1) a glass chamber containing the sample ($V = 8$ mL), that is placed inside an aluminum block sited on top of a heating and stirring plate; (2) a glass condenser at the top of the chamber where the temperature is kept constant by means of a thermostatic bath; and (3) a liquid injection system, temperature probes and pressure line connections. A Büchi V-700 vacuum pump and a pressure controller unit are used to control and monitor the systems pressure that is measured by a Baratron type capacitance Manometer (MKS model 728A, $u_r(p) = 0.005$). The temperature of the liquid

phase inside the ebullimeter, is measured by means of a fast response glass sealed thermocouple type K ($u(T) = 1$ K), calibrated previously against a calibrated platinum resistance thermometer, SPRT100 (Fluke-Hart Scientific 1529 Chub-E4), traceable to the National Institute of Standards and Technology (NIST), with an uncertainty lower than 2×10^{-2} .

During the measurements, the equilibrium was assumed when the temperature remained constant, i.e. with a temperature drift lower than 0.05 K min^{-1} for at least 5 min. The liquid's phase was then sampled, and its composition determined through refractive index measurements using an Anton Paar Abbemat 500 refractometer (2×10^{-5} nD).

3. Thermodynamic model

3.1. Soft-SAFT EoS

Although widely used in the natural gas industry, cubic EoSs and several activity coefficient models exhibit limited accuracy when used to describe complex systems containing strong associating and/or polar fluids. Among such fluids, water is known by its complex and highly non-ideal behavior despite its apparently simple structure. This complex behavior is partially explained by its associating character, i.e. the presence of strong, highly directional, short-range attractive forces that are responsible for most of the physicochemical anomalies found in water, such as the maximum on density [22]. Consequently, most models proposed up to date are unable to accurately describe a large number of different thermodynamic properties and phase behavior of pure water and water-containing systems, unless extensive amounts of experimental data are available to fit the model to a given set of conditions [22].

To improve the description of the thermodynamic behavior of associating systems, a first-order thermodynamic perturbation theory (TPT1) of association was proposed by Wertheim [23–26] allowing the development of the so-called Statistical Associating Fluid Theory (SAFT) EoS. SAFT EoSs are a class of engineering-oriented equations of state based on statistical mechanics concepts, that using Wertheim's TPT1, include a term explicitly accounting for highly directional, short range forces such as hydrogen bonding, thus standing suitable to describe water-containing systems [27,28]. In SAFT, molecules are usually modeled as a number of equal-sized spherical segments, or monomers, that are covalently bonded forming chains that interact with each other according to a certain intermolecular potential. If the compound is associating, association sites (usually modeled by square-well sites embedded into the monomer spheres) are added into some of the segments in the chain to reproduce those interactions. Then, according to equation (1), the residual Helmholtz energy of the system is obtained as a sum of different terms, each accounting for a specific structural or energetic contribution.

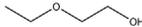
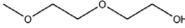
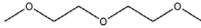
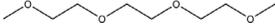
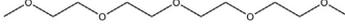
$$A^{res} = A^{total} - A^{ideal} = A^{ref} + A^{chain} + A^{assoc} \quad (1)$$

In equation (1), the superscripts *total*, *res* and *ideal* represent the total, residual, and ideal Helmholtz energy of the system. A^{ref} represents the energy contribution of the reference fluid due to the interactions between the individual monomers, A^{chain} accounts for the formation of chains by the covalent bonding of monomers, while A^{assoc} is a term that describes the presence of anisotropic, short-range and strong attractive forces such as hydrogen bonding. Both A^{chain} and A^{assoc} are based on the TPT1 by Wertheim [23–26] and are kept essentially unchanged across the different variants of SAFT, whose difference relies mainly on the reference term.

Considering that the soft-SAFT variant of the equation,

Table 1

Name, chemical structure, CAS number, molecular weight (Mw), water content (H₂O wt.), purity and supplier of the glycol ethers studied in this work.

Glycol ether	Chemical structure
Ethylene glycol ethyl ether (EGEE) CAS: 110-80-5; Mw = 90.12 g mol ⁻¹ ; H ₂ O wt. = 0.0041 ^a ; purity = 99 wt%. Acquired from Panreac.	
Diethylene glycol methyl ether (DEGME) CAS: 111-77-3; Mw = 120.15 g mol ⁻¹ ; H ₂ O wt = 0.0015 ^a ; purity = 99 wt%. Acquired from Acos Organic.	
Diethylene glycol ethyl ether (DEGEE) CAS: 111-90-0; Mw = 134.17 g mol ⁻¹ ; H ₂ O wt = 0.0003 ^a ; purity = 98 wt%. Acquired from Acros Organic.	
Diethylene glycol dimethyl ether (DEGDME) CAS: 111-96-6; Mw = 134.17 g mol ⁻¹ ; H ₂ O wt = 0.0160 ^a ; purity = 99.5 wt%. Acquired from Sigma Aldrich.	
Triethylene glycol dimethyl ether (TriEGDME) CAS: 112-49-2; Mw = 178.23 g mol ⁻¹ ; H ₂ O wt = 0.0002 ^a ; purity = 99 wt%. Acquired from Alfa Aesar	
Tetraethylene glycol dimethyl ether (TeEGDME) CAS: 143-24-8; Mw = 222.28 g mol ⁻¹ ; H ₂ O wt = 0.0002 ^a ; purity = 99 wt%. Acquired from Acros Organics	

^a Compound dried using 3 Å molecular sieves.

developed by Vega and co-workers [15,29], has been applied successfully to the description of thermophysical properties and phase behavior of systems composed by a diversity of compounds such as nitriles [30], amines [31–33], ionic liquids [34–36], deep eutectic solvents [37–39], refrigerants [40], CO₂ [10,31], and of particular relevance to this work, polyethers [16,17] and water [18,22,41], it is used in this work to correlate the new experimental data measured in this work and further used as a predictive tool for other conditions.

In soft-SAFT, a Lennard-Jones (LJ) fluid that accounts for both repulsive and attractive forces is chosen as reference fluid [42]. Therefore, to fully describe a non-associating component three molecular parameters are required by the soft-SAFT EoS, namely the LJ diameter of the spherical segments, σ , the dispersive energy ruling the monomer-monomer interactions, ϵ and the number of monomers in the molecule, m , also known as the chain length. For associating components, an association scheme specifying the number/type of association sites to be added to the molecules and the type of interactions allowed between different sites has to be specified a priori. Two additional molecular parameters are necessary to characterize the energy (ϵ^{HB}) and volume (κ^{HB}) of the bonding sites for associating molecules. All the molecular parameters are typically regressed from pure fluids VLE data, namely the vapor pressures and saturated liquid densities but, if such data is not available, as it is the case of compounds with high melting points or low vapor pressures, alternative methodologies can be used [39].

The chain and association terms in equation (1) are readily written for mixtures. The extension of the reference term to mixtures is carried out by applying the van der Waals one-fluid theory where the unlike size (σ_{ij}) and energy (ϵ_{ij}) parameters are retrieved from the Lorentz-Berthelot mixing rules, expressed as equations 2-3:

$$\sigma_{ij} = \eta_{ij} \frac{\sigma_{ii} + \sigma_{jj}}{2} \quad (2)$$

$$\epsilon_{ij} = \xi_{ij} \sqrt{\epsilon_{ii} \epsilon_{jj}} \quad (3)$$

These equations contain two adjustable binary interaction parameters (BIPs), η_{ij} and ξ_{ij} , correcting the size and energy of the interactions between a molecule type i and a molecule type j that can be fitted to binary experimental data if predictions from the pure-component parameters ($\eta_{ij} = \xi_{ij} = 1$) are not satisfactory. Hence, these BIPs account, somehow, for the non-ideality of the mixture.

Similarly, if the system contains more than one associating component, cross-association energies and volumes of interaction between a site type α in a chain of component i and a site type β in a chain of component j are required, those being obtained from appropriate combining rules. In soft-SAFT the following combining rules are usually applied in the association term:

$$\epsilon_{ij}^{\alpha\beta} = \sqrt{\epsilon_i^{\alpha} \epsilon_j^{\beta}} \quad (4)$$

$$\kappa_{ij}^{\alpha\beta} = \left(\frac{\sqrt[3]{\kappa_i^{\alpha}} + \sqrt[3]{\kappa_j^{\beta}}}{2} \right)^3 \quad (5)$$

Notice that equations 4-5 are averages from the values of the pure components, hence, no fitting to the mixtures data is performed when using them.

3.2. Coarse-grain molecular models

The accuracy of SAFT-type EoSs relies on the choice of reliable coarse-grain models that comprise both the selection of a proper

Table 2
Soft-SAFT molecular parameters for the compounds studied in this work [17,41].

	m	$\sigma/\text{\AA}$	$\epsilon/k_B/K$	$\epsilon^{HB}/k_B/K$	$\kappa^{HB}/\text{\AA}^3$
EGEE	2.705	3.721	294.87	3450	2600
DEGME	2.995	3.889	330.50	3450	2600
DEGEE	3.165	4.009	331.00	3450	2600
DEGDME	3.300	3.955	308.15	—	—
TriEGDME	4.021	4.039	318.12	—	—
TeEGDME	4.696	4.107	322.68	—	—
Water	1.000	3.154	365.00	2388	2932

number of associating sites, the association scheme and the definition of all pure-component parameters. These coarse-grain models should capture most of the basic physical features of the compounds under investigation, and follow expected trends when comparing them with other molecular models (such as molecular simulations [43]) and among chemical families.

A molecular model for polyethers was proposed in our previous works [16,17], in the framework of the soft-SAFT EoS. This model accurately reproduced the VLE, high-pressure densities (ρpT), isothermal compressibility (k_T) and isobaric thermal expansivities (α_p) of both glycols and glymes. Moreover, given the transferability character of SAFT-type EoSs, and the physically meaningful parameterization that was carried, correlations for the non-associating parameters as a function of the chain length were proposed so that the molecular parameters characterizing a polyether, of any molecular weight, could be estimated, even in the absence of experimental data for the pure compound.

Within this model, and as is commonly done with SAFT-type EoSs [44], a polyether is represented as a homonuclear chainlike molecule where only the hydrogen bonding character of the hydroxyl end groups is explicitly accounted for by the inclusion of square well association sites. Hence, one association site (type A) per hydroxyl end-group is added to the core of the molecule, embedded off-center in one of the chains segments, with AA interactions being allowed in the pure fluid. Contrarily to previous models, as for example the more detailed model of alkan-1-ols [45] or water [41], in the coarse-grain model used in this work the different associative interactions within the hydroxyl group are not discriminated. Instead, a dual nature of the association site is considered so that it is able to interact both with positive or negative association sites present in other molecules. Despite being a clear simplification of the model, the introduction of dual association character of the sites has been demonstrated to provide an enhanced transferability of the models while ensuring an equally satisfying accuracy [16,17,46,47].

The six glymes studied in this work were previously used to parameterize our coarse-grain model for polyethers, hence, the necessary soft-SAFT molecular parameters for the calculations to be performed in this work were available from our previous work and were used here without further refinement. They are summarized in Table 2 for completeness.

Concerning the water molecules, they are modeled following the work of Vega et al. [41] that considers a LJ sphere with a 4C association scheme, according to the Huang and Radosz nomenclature [48,49]. Under this association scheme, two positive association sites type "B" are used to represent the hydrogen atoms while two negative sites type "C" are used to mimic the lone electron pairs of the oxygen atom. The correspondent molecular parameters (fitted at temperatures near ambient conditions) are also reported in Table 2.

When studying the glymes + water binary mixtures, cross-association interactions have to be considered between water and mono-alkyl glymes (those containing a terminal -OH group), with the required cross-association parameters being obtained in a fully

Table 3
Binary interaction parameters glyme/water, and the deviations between the model correlations and the experimental data.

Compounds (g)	$\xi_{g\text{-water}}$	AAD(T)/K	%AAD(γ)
EGEE	1.105	0.814	18.7
DEGME	1.145	1.10	4.53
DEGEE	1.170	0.873	4.24
DEGDME	1.210	0.975	9.31
TriEGDME	1.220	1.27	5.04
TeEGDME	1.220	1.13	4.34

$$\text{AAD}(T)/K = \frac{1}{N} \sum_{i=1}^N T_i^{\text{EoS}} - T_i^{\text{exp}} \%$$

$$\text{AAD}(\gamma) = \frac{1}{N} \sum_{i=1}^N \frac{100 \times |\gamma_i^{\text{calc}} - \gamma_i^{\text{exp}}|}{\gamma_i^{\text{exp}}}$$

predictive manner using equations 4-5.

4. Results and discussion

The isobaric VLE for the binary mixtures composed of water and the selected glymes were measured at three different pressures, namely 0.10, 0.07 and 0.05 MPa and glymes mole fractions up to 0.7, corresponding to equilibrium temperatures up to 395 K. The results obtained are presented in Fig. 1 and reported in the tabular form in Tables S1–S6 (in Supporting Information). For glycol ether mole fractions higher than 0.7 the low amount of volatile compound at the liquid phase leads to unstable experimental conditions hampering the correct description of the complete phase diagram. Nonetheless, the excellent extrapolative ability of soft-SAFT allows to infer about the behavior of the system in the whole concentration range, as will be shown later in this work.

The experimental results obtained in this work show that, as expected, the mixtures' boiling temperature increases with the glymes mole fraction. In the water-rich region ($x_w = 0.8-1.0$), there is only a slight increase of the equilibrium temperature as glyme is added to the system. On the contrary, in the glycol ether-rich phase, a steep increase of the systems temperature towards the boiling temperature of the pure glyme can be observed.

As mentioned in the **Introduction**, despite the interest of using glycol ethers in aqueous media, there is a lack of experimental data concerning the VLE of such systems. From the binary mixtures studied in this work, EGEE + water is the most widely studied. Dominik et al. [50] and Bubnova et al. [51] reported the isobaric VLE of EGEE + water in the entire composition range at atmospheric pressure while Chiavone-Filho et al. [14] measured the isothermal VLE of binary mixtures composed of water and five different low-molecular weight glycol ethers including EGEE, at two different temperatures (343 and 363 K). The literature values corresponding to any of the pressures investigated in this work are plotted in Fig. 2 (left) as unfilled symbols and, as can be observed, an excellent agreement is found between our data and those reported in the literature, validating the adopted experimental methodology.

For the remaining systems depicted in Fig. 2 (right), experimental data could only be found in the work of Sartakova and co-authors [52], for DEGDME at atmospheric pressure. Similar to EGEE, a good agreement with our data and soft-SAFT calculations is observed.

Given the complexity of most aqueous systems, thermodynamic models are usually unable to correctly predict their thermodynamic behavior. In this work, when the soft-SAFT EoSs was used in its purely predictive form (not using BIPs), the model predicts immiscibility of the two compounds in the liquid phase, a behavior contrary to the one observed experimentally. Furthermore, the

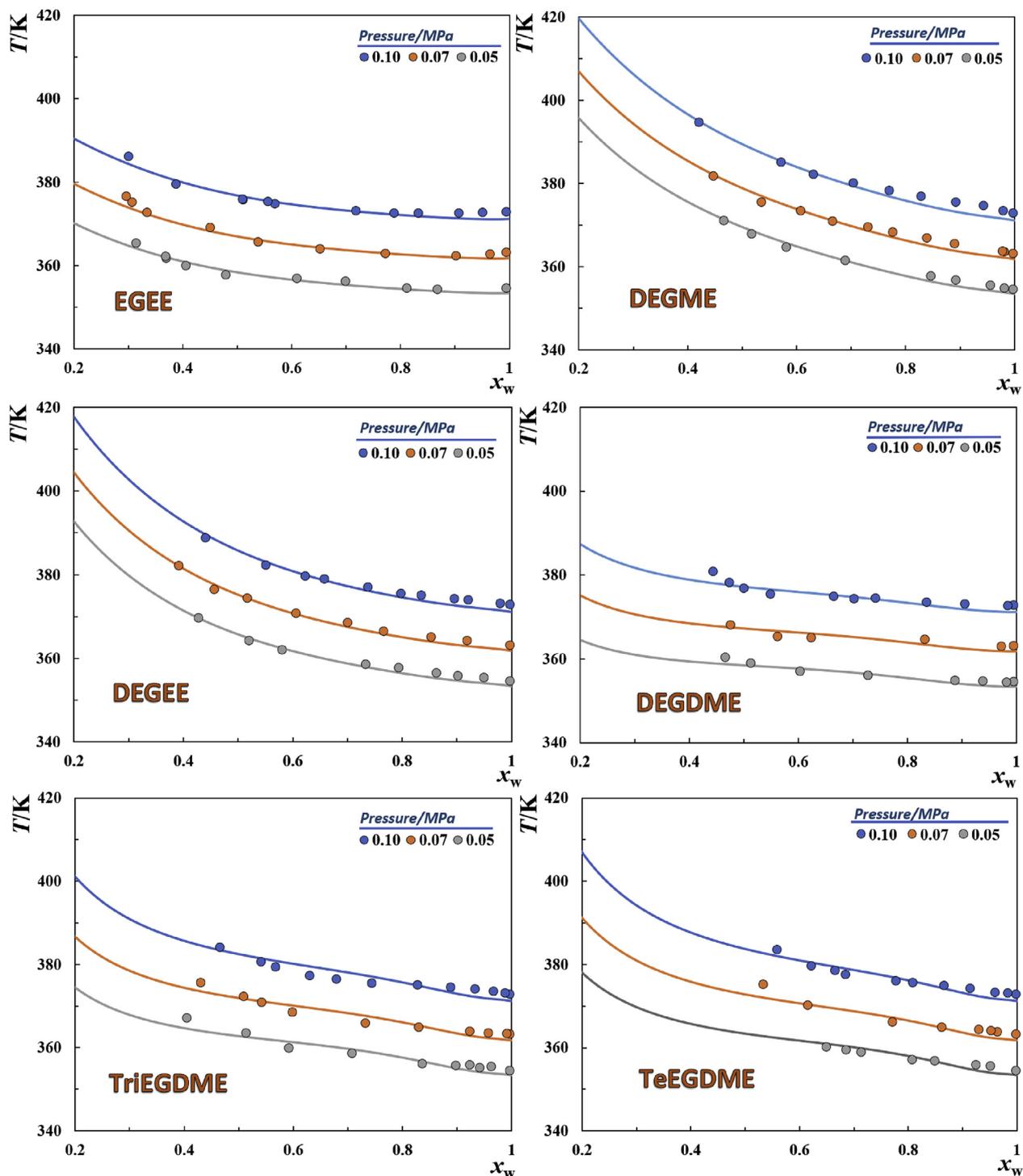


Fig. 1. Isobaric temperature-composition phase diagrams of the binary glycol ether + water mixtures. The symbols represent the experimental data measured in this work while the solid lines represent the soft-SAFT results using the binary interaction parameters from Table 3.

degree of immiscibility between the studied glymes and water clearly increase for the di-alkyl glymes (i.e. glycol ethers without the terminal hydroxyl group). An explanation for such behavior is the absence of association sites in the simplified coarse-grain model of these molecules used in this work, that implies that the difference between the pure component properties of *n*-alkanes and di-alkyl glymes, i.e. the role of the inner ethylene oxide units, was only implicitly captured by the specific values of the molecular

parameters, albeit obtained through a careful and methodical parameterization (see Ref. [17]). However, this approach, which has also been used with other SAFT variants [53], seems clearly insufficient to capture the difference between these two types of molecules when present in an aqueous medium, urging the development of more robust and accurate models of glycol ethers and highlighting the well-known deficiencies of most models when dealing with water-containing systems.

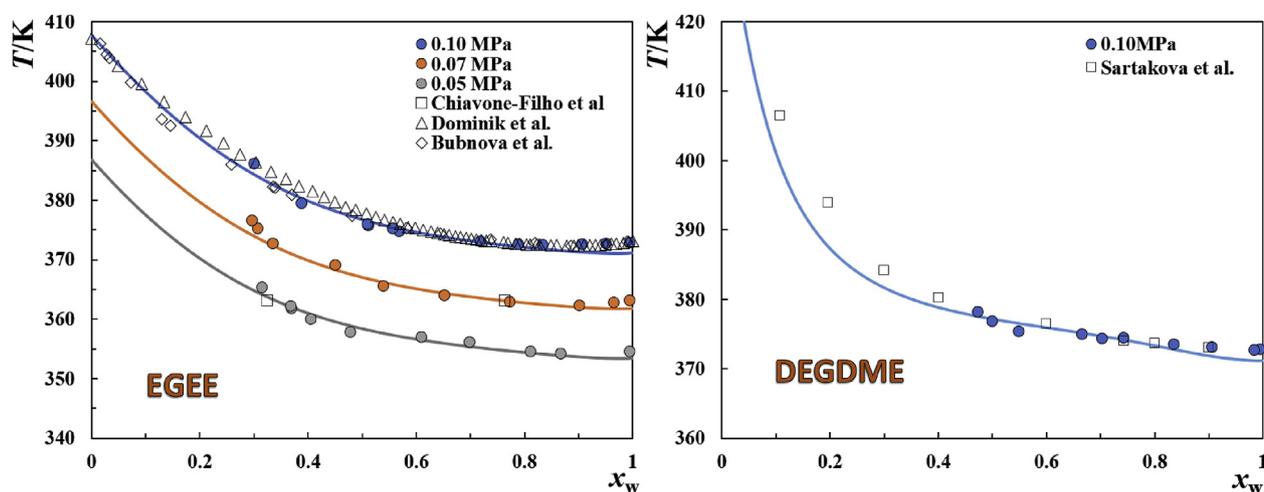


Fig. 2. Comparison between experimental data from this work and data retrieved from literature for EGEE and DEGDME [14,50–52]. The solid lines represent the soft-SAFT calculations using the binary interaction parameters from Table 3.

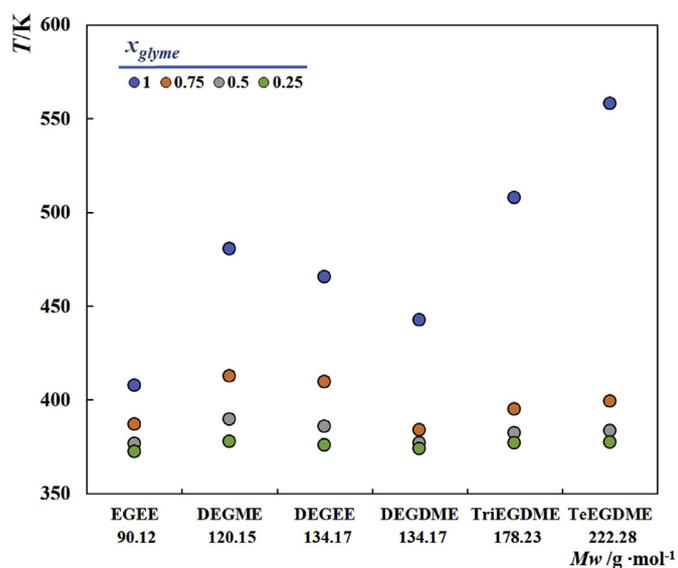


Fig. 3. Boiling temperatures (@1 atm) of the pure glycol ethers studied in this work and the equilibrium temperature of their aqueous solutions at different glyme mole fractions as calculated by the soft-SAFT EoS using the BIPs from Table 3.

Consequently, in order to accurately describe most aqueous systems, one or more binary parameters, correcting the cross-interaction parameters obtained from the Lorentz-Berthelot mixing rules, are required. As already mentioned, these BIPs are known to correct the non-ideality of the mixtures on a coarse-grained manner, as all non-ideality are comprised into these BPs. In this work, a state-independent BIP, fitted to the intermediate isobar at 0.07 MPa, is used to correct the mixtures dispersive energy (ξ in equation (3)), while no corrections are considered for the size parameter. As depicted in Fig. 1, an excellent description is obtained for all the studied systems with average absolute deviations ($AAD = \frac{1}{N} \sum T_i^{EoS} - T_i^{exp}$) in temperature lower than 1.30 K. The AAD values for the different systems and the values of the BIPs are reported in Table 3 and, as can be observed, all the binary parameters were found to be higher than unity, suggesting that the interactions between the glycol ethers and water unfavorable versus the glycol ether-glycol ether and water-water interactions, are

underestimated by the model.

The isobars calculated by soft-SAFT using the appropriate BIP for the systems with EGEE and DEGDME are also depicted in Fig. 2, where the good agreement with the literature data in the entire composition range, demonstrates the excellent extrapolative ability of the model.

In our previous work [18], a state-independent BIP, correcting the unlike energy between LJ segments, ensured an accurate description of the experimental data for the aqueous mixtures with the first four members of the glycol series (mono-up to tetra-ethylene glycol). This BIP was shown to increase with the glycols' molecular weight until reaching a plateau for polyethylene glycol (PEG) 400, remaining constant for higher chain length polymers. This allowed the successful prediction of water activities in PEGs of molecular weight up to 6000 g/mol although the molecular model had been built using experimental data for glycols with a molecular weight lower than 300 g/mol. Similarly, in this work, the values of the BIP increase with the chain length of the glyme until reaching an asymptotic value of 1.22 for TeEGDME. Although there is no experimental data for higher members in order to evaluate the predictive ability of the model, the common root of both models suggest that this model can be used to successfully predict the VLE of heavier glymes in water than those studied in this work.

In Fig. 3, the boiling temperatures of the pure glymes and that of their aqueous mixtures at three different compositions (glyme mole fraction of 0.25, 0.50 and 0.75) as calculated by the soft-SAFT EoS using the BIPs from Table 3 are reported. The data plotted on this figure suggests that the mixtures boiling temperatures increase with the glymes chain length, as expected due to an increase of both the van der Waals dispersion forces and the polar interactions involving the ethylene oxide groups, with the temperature increasing in the following order DEGDME < TriEGDME < TeEGDME. However, the replacement of a terminal methyl group by an ethyl group and the removal of the terminal hydroxyl group of mono-alkyl glymes have the opposite effect, lowering the equilibrium temperature. If the latter effect is relatively easy to understand due to the lower number of hydrogen bonds that can be established once a highly associative functional group is removed, the former is more convoluted with a possible explanation being that the existence of a bulkier terminal group hinders the otherwise easy access of water molecules to the inner ethylene oxide groups, diminishing the magnitude of the cross-interactions.

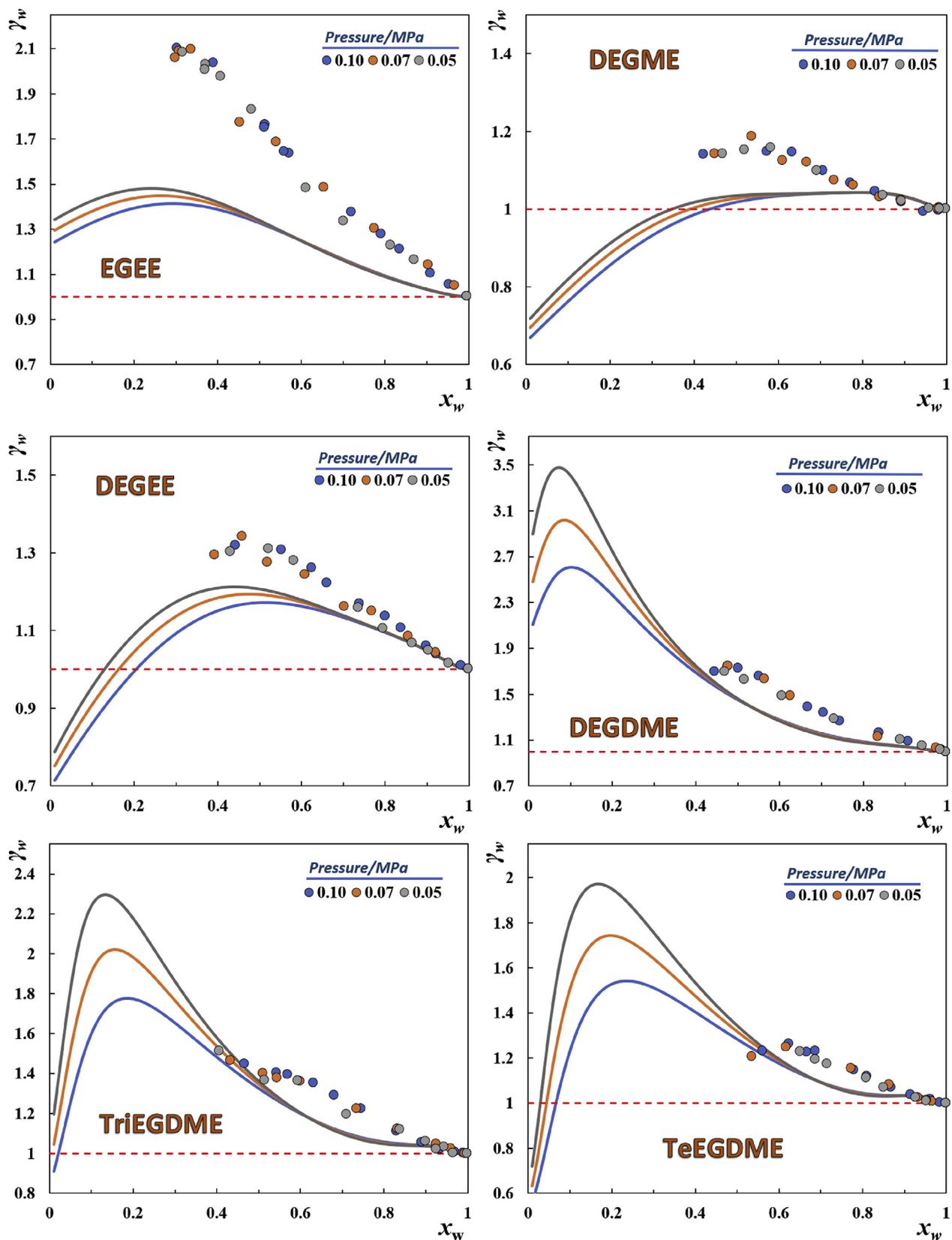


Fig. 4. Water activity coefficients for the studied binary systems at 0.1, 0.07 and 0.05 MPa. Symbols represent estimates obtained from the experimental boiling temperatures using equation (7) while the solid lines depict the soft-SAFT results using the BIPs reported in Table 3 and equation (6). The red dashed lines depict the ideal behavior ($\gamma_w = 1$).

From the experimental boiling temperatures, the water activity coefficients (γ_w) can be estimated using the modified Raoult's law and used to rationalize the non-ideality of these systems. The modified Raoult's law is expressed by:

$$\gamma_w = \frac{y_w \times \phi_w^V \times p}{x_w \times \phi_w^* \times p_w^*} \quad (6)$$

where x_w and y_w are the water mole fractions in the liquid and vapor phase, ϕ_w^* and ϕ_w^V are the water fugacity coefficients at the saturation conditions and in the vapor phase, p is the system pressure and p_w^* is the vapor pressure of pure water at the system temperature.

At the low pressures investigated in this work, it can be assumed that the fugacity coefficients are very close to unity. Moreover, given the lower volatility of glycol ethers compared to water, in the range of compositions investigated in this work, the vapor phase is mostly composed of water ($y_w \cong 1$) allowing equation (6) to be further simplified as:

$$\gamma_w = \frac{p}{x_w p_w^*} \quad (7)$$

The water activity coefficients estimated from the experimental measurements, using equation (7), are plotted in Fig. 4 along with the values obtained from the soft-SAFT EoS, using the more rigorous equation (6) and the BIPs from Table 3. As can be observed, a reasonable agreement between the experimental estimates and the modelling results is found for most systems, despite the simplifications considered when treating the experimental data. The average absolute relative deviations (%)

$$\text{AAD} = \frac{1}{N} \sum_{i=1}^N \left(\frac{100 \times |\gamma_i^{\text{calc}} - \gamma_i^{\text{exp}}|}{\gamma_i^{\text{exp}}} \right)$$

between the two sets of data are reported in Table 3 and highlight the high deviations observed for the lighter glyme investigated. This is expected, considering the high volatility of EGEE and the consequent increase of the glyme concentration in the vapor phase that can no longer be neglected as done when using equation (7) for the experimental data.

Contrarily to what was observed in the previous work on the isobaric VLE of binary mixtures glycols + water, the water activity coefficients were found to be higher than unity in the whole concentration range investigated, denoting the existence of weaker interactions in the mixture than those observed in pure water, as also inferred from the values of the energy BIPs greater than unity. For the mono-alkyl glymes, the water activity coefficients decrease with the increase of the glymes chain length (e.g. $\gamma_w(\text{DEGME}) < \gamma_w(\text{EGEE})$) probably due to the increase of the number of the ethylene oxide groups that can interact favorably with the water molecules. Conversely, following the same reasoning as for the decrease of the boiling temperatures, the replacement of a terminal methyl group by an ethyl group increases the water activity coefficients. Furthermore, the water activity coefficients in the systems with di-alkyl glymes suggest that the removal of the terminal hydroxyl group reduces, as expected, the interactions with water, translated into an increase of the water activity coefficients (e.g. $\gamma_w(\text{DEGDME}) > \gamma_w(\text{DEGEE})$).

Although there is no experimental data in the glycol rich region of the vapor-liquid phase diagram, the soft-SAFT EoS was used to predict the water activity coefficients in the whole concentration range (water mole fractions ranging from 0.01 to 1) and the results are depicted in Fig. 4. As inferred from the figure, there is a maximum on the water activity coefficients of every system whose value decreases when increasing the chain length of the glymes, adding a terminal hydroxyl group, or through the replacement of a terminal ethyl group by a methyl counterpart. This agrees with the

effect of these structural changes on the boiling temperatures previously discussed and shown in Fig. 3.

5. Conclusions

In this work, a combined theoretical/experimental approach has been used to study the isobaric VLE of six binary mixtures of water with different glycol ethers, namely EGEE, DEGME, DEGEE, DEGDME, TriEGDME, and TeEGDME.

The boiling temperatures for the different mixtures were measured experimentally using an isobaric microebulliometer at three different pressures and were here reported for the first time.

Using a previously developed soft-SAFT coarse-grain model for polyethers, the experimental data was successfully correlated (AAD lower than 1.30 K) using a state-independent binary parameter, correcting the mixtures dispersive energy. The values of the binary parameters were found to be greater than unity, denoting the unfavorable interactions between the glymes and the water compared to the glyme-glyme and water-water interactions. Furthermore, and as previously observed for glycols, the binary parameter slightly increases with the glymes molecular weight until reaching an asymptotic value that can be used to provide reliable predictions for the VLE of mixtures containing heavier compounds.

From the experimental data, water activity coefficients were estimated from the modified Raoult's law assuming that the glymes content in the vapor phase is negligible. Simultaneously, more rigorous values of the water activity coefficients were also calculated using the soft-SAFT EoS with the corresponding binary parameters providing a reasonable agreement between the two sets of data with AAD lower than 1.5 K in temperature and AARD around 5% in the activity coefficients. Largest deviations were obtained for the mixture with EGEE, the lighter glyme, as the assumption of non-negligible content in the vapor phase is not valid in this case, due to its higher volatility, compared to the other investigated glymes.

The use of a reliable thermodynamic model to describe the experimental data allowed to infer about the effect of different structural changes on both the boiling temperatures and water activity coefficients in the whole concentration range (water mole fractions ranging from 0.01 to 1) despite experimental measurements were limited to water mole fractions higher than 0.3 to ensure the systems stability. Both, the replacement of a terminal ethyl group by a shorter methyl group or the removal of a terminal hydroxyl group of the mono-alkyl glymes results in a decrease of the equilibrium temperature, translated into an increase of the water activity coefficients. This is due to the decrease of the magnitude of hydrogen bonds established between the two components that seem to be well captured by the model.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRedit authorship contribution statement

Emanuel A. Crespo: Investigation, Data curation, Writing - original draft. **Naima Chouireb:** Investigation, Writing - original draft. **O. Tafat Igoudjilene:** Supervision, Validation. **Lourdes F. Vega:** Supervision, Validation, Writing - review & editing. **Pedro J. Carvalho:** Conceptualization, Supervision, Validation, Writing - review & editing. **João A.P. Coutinho:** Supervision, Writing - review & editing.

Acknowledgments

This work was developed within the scope of the project CICECO - Aveiro Institute of Materials, FCT Ref. UID/CTM/50011/2019, financed by national funds through the FCT/MCTES, and when appropriate co-financed by FEDER under the PT2020 Partnership Agreement. This work was funded by PARTEX OIL & GAS. E. A. Crespo acknowledges FCT for the Ph.D. Grant SFRH/BD/130870/2017. P. J. Carvalho also acknowledges FCT for a contract under the Investigador FCT 2015, contract number IF/00758/2015. L.F. Vega acknowledges support from Khalifa University of Science and Technology through project RC2-2019-007.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.fluid.2020.112547>.

References

- [1] M.I. Stewart, Gas sweetening, in: Surf. Prod. Oper., third ed., Gulf Professional Publishing, Boston, 2014 <https://doi.org/10.1016/B978-0-12-382207-9.00009-3>, 433–539.
- [2] S.F. Sciamanna, S. Lynn, Solubility of hydrogen sulfide, sulfur dioxide, carbon dioxide, propane, and n-butane in poly(glycol ethers), Ind. Eng. Chem. Res. 27 (1988) 492–499, <https://doi.org/10.1021/ie00075a020>.
- [3] A. Henni, A.E. Mather, The solubility of CO₂ in triethylene glycol monomethyl ether, Can. J. Chem. Eng. 73 (1995) 156–158, <https://doi.org/10.1002/cjce.5450730119>.
- [4] I. Gainar, G. Anitescu, The solubility of CO₂, N₂ and H₂ in a mixture of dimethylether polyethylene glycols at high pressures, Fluid Phase Equil. 109 (1995) 281–289, [https://doi.org/10.1016/0378-3812\(95\)02729-X](https://doi.org/10.1016/0378-3812(95)02729-X).
- [5] K.A.G. Schmidt, A.E. Mather, Solubility of sulphur dioxide in mixed polyethylene glycol dimethyl ethers, Can. J. Chem. Eng. 79 (2001) 946–960, <https://doi.org/10.1002/cjce.5450790613>.
- [6] A. Henni, P. Tontiwachwuthikul, A. Chakma, Solubilities of carbon dioxide in polyethylene glycol ethers, Can. J. Chem. Eng. 83 (2005) 358–361, <https://doi.org/10.1002/cjce.5450830224>.
- [7] A.-L. Revelli, F. Mutelet, J.-N. Jaubert, High carbon dioxide solubilities in imidazolium-based ionic liquids and in poly(ethylene glycol) dimethyl ether, J. Phys. Chem. B 114 (2010) 12908–12913, <https://doi.org/10.1021/jp1057989>.
- [8] D. Kodama, M. Kanakubo, M. Kokubo, S. Hashimoto, H. Nanjo, M. Kato, Density, viscosity, and solubility of carbon dioxide in glymes, Fluid Phase Equil. 302 (2011) 103–108, <https://doi.org/10.1016/j.fluid.2010.08.014>.
- [9] A.V. Rayer, A. Henni, P. Tontiwachwuthikul, High pressure physical solubility of carbon dioxide (CO₂) in mixed polyethylene glycol dimethyl ethers (Genosorb 1753), Can. J. Chem. Eng. 90 (2011) 576–583, <https://doi.org/10.1002/cjce.20615>.
- [10] M. Amaral, E.A. Crespo, C. Dariva, L.F. Vega, P.J. Carvalho, J.A.P. Coutinho, High-pressure solubility of CO₂ in glymes, Fuel 219 (2018) 120–125, <https://doi.org/10.1016/j.fuel.2018.01.084>.
- [11] U.O.P. Llc, Selexol Process, www.Uop.Com, 2007.
- [12] J. Ameen, S.A. Furbush, Solvent Composition Useful in Acid Gas Removal from Gas Mixtures, US3737392, United States Patent Office, 1973.
- [13] M. Pastor-Belda, N. Campillo, M. Hernández-Córdoba, P. Viñas, Gas chromatography with mass spectrometry for the quantification of ethylene glycol ethers in different household cleaning products, J. Separ. Sci. 39 (2016) 2292–2299, <https://doi.org/10.1002/jssc.201600180>.
- [14] O. Chivone-Filho, P. Proust, P. Rasmussen, Vapor-liquid equilibria for glycol ether + water systems, J. Chem. Eng. Data 38 (1993) 128–131, <https://doi.org/10.1021/je00009a031>.
- [15] F.J. Blas, L.F. Vega, Thermodynamic behaviour of homonuclear and heteronuclear Lennard-Jones chains with association sites from simulation and theory, Mol. Phys. 92 (1997) 135–150, <https://doi.org/10.1080/002689797170707>.
- [16] E.A. Crespo, J.M.L. Costa, Z.B.M.A. Hanafiah, K.A. Kurnia, M.B. Oliveira, F. Llovel, L.F. Vega, P.J. Carvalho, J.A.P. Coutinho, New measurements and modeling of high pressure thermodynamic properties of glycols, Fluid Phase Equil. 436 (2017) 113–123, <https://doi.org/10.1016/j.fluid.2017.01.003>.
- [17] P. Navarro, E.A. Crespo, J.M.L. Costa, F. Llovel, J. García, F. Rodríguez, P.J. Carvalho, L.F. Vega, J.A.P. Coutinho, New experimental data and modeling of glymes: toward the development of a predictive model for polyethers, Ind. Eng. Chem. Res. 56 (2017) 7830–7844, <https://doi.org/10.1021/acs.iecr.7b01532>.
- [18] N. Chouireb, E.A. Crespo, L.M.C. Pereira, O. Tafat-Igoudjilene, L.F. Vega, J.A.P. Coutinho, P.J. Carvalho, Measurement and modeling of isobaric vapor-liquid equilibrium of water + glycols, J. Chem. Eng. Data 63 (2018) 2394–2401, <https://doi.org/10.1021/acs.jced.7b00945>.
- [19] P.J. Carvalho, I. Khan, A. Morais, J.F.O. Granjo, N.M.C. Oliveira, L.M.N.B.F. Santos, J.A.P. Coutinho, A new microbulliometer for the measurement of the vapor-liquid equilibrium of ionic liquid systems, Fluid Phase Equil. 354 (2013) 156–165, <https://doi.org/10.1016/j.fluid.2013.06.015>.
- [20] I. Khan, M.L.S. Batista, P.J. Carvalho, L.M.N.B.F. Santos, J.R.B. Gomes, J.A.P. Coutinho, Vapor-liquid equilibria of imidazolium ionic liquids with cyano containing anions with water and ethanol, J. Phys. Chem. B 119 (2015) 10287–10303, <https://doi.org/10.1021/acs.jpcc.5b03324>.
- [21] M. Stuckenholtz, E.A. Crespo, L.F. Vega, P.J. Carvalho, J.A.P. Coutinho, W.H. Schroer, J. Kiefer, B. Rathke, Vapor liquid equilibria of binary mixtures of 1-Butyl-3-methylimidazolium triflate (C4mimTfO) and molecular solvents: N-alkyl alcohols and water, J. Phys. Chem. B 122 (2018) 6017–6032, <https://doi.org/10.1021/acs.jpcc.8b03278>.
- [22] L.F. Vega, F. Llovel, Review and new insights into the application of molecular-based equations of state to water and aqueous solutions, Fluid Phase Equil. 416 (2016) 150–173, <https://doi.org/10.1016/j.fluid.2016.01.024>.
- [23] M.S. Wertheim, Fluids with highly directional attractive forces. I. Statistical thermodynamics, J. Stat. Phys. 35 (1984) 19–34, <https://doi.org/10.1007/BF01017362>.
- [24] M.S. Wertheim, Fluids with highly directional attractive forces. II. Thermodynamic perturbation theory and integral equations, J. Stat. Phys. 35 (1984) 35–47, <https://doi.org/10.1007/BF01017363>.
- [25] M.S. Wertheim, Fluids with highly directional attractive forces. III. Multiple attraction sites, J. Stat. Phys. 42 (1986) 459–476, <https://doi.org/10.1007/BF01127721>.
- [26] M.S. Wertheim, Fluids with highly directional attractive forces. IV. Equilibrium polymerization, J. Stat. Phys. 42 (1986) 477–492, <https://doi.org/10.1007/BF01127722>.
- [27] W.G. Chapman, K.E. Gubbins, G. Jackson, M. Radosz, SAFT: equation-of-state solution model for associating fluids, Fluid Phase Equil. 52 (1989) 31–38, [https://doi.org/10.1016/0378-3812\(89\)80308-5](https://doi.org/10.1016/0378-3812(89)80308-5).
- [28] W.G. Chapman, K.E. Gubbins, G. Jackson, M. Radosz, New reference equation of state for associating liquids, Ind. Eng. Chem. Res. 29 (1990) 1709–1721, <https://doi.org/10.1021/ie00104a021>.
- [29] F.J. Blas, L.F. Vega, Prediction of binary and ternary diagrams using the statistical associating fluid theory (SAFT) equation of state, Ind. Eng. Chem. Res. 37 (1998) 660–674, <https://doi.org/10.1021/ie970449+>.
- [30] A. Belkadi, M.K. Hadji-Kali, F. Llovel, V. Gerbaud, L.F. Vega, Soft-SAFT modeling of vapor-liquid equilibria of nitriles and their mixtures, Fluid Phase Equil. 289 (2010) 191–200, <https://doi.org/10.1016/j.fluid.2009.12.012>.
- [31] J.O. Lloret, L.F. Vega, F. Llovel, A consistent and transferable thermodynamic model to accurately describe CO₂ capture with monoethanolamine, J. CO₂ Util. 21 (2017) 521–533, <https://doi.org/10.1016/j.jcou.2017.08.018>.
- [32] L.M.C. Pereira, F. Llovel, L.F. Vega, Thermodynamic characterisation of aqueous alkanolamine and amine solutions for acid gas processing by transferable molecular models, Appl. Energy 222 (2018) 687–703, <https://doi.org/10.1016/j.apenergy.2018.04.021>.
- [33] L.M.C. Pereira, L.F. Vega, A systematic approach for the thermodynamic modelling of CO₂-amine absorption process using molecular-based models, Appl. Energy 232 (2018) 273–291, <https://doi.org/10.1016/j.apenergy.2018.09.189>.
- [34] J.S. Andreu, L.F. Vega, Capturing the solubility behavior of CO₂ in ionic liquids by a simple model, J. Phys. Chem. C 111 (2007) 16028–16034, <https://doi.org/10.1021/jp074353x>.
- [35] J.S. Andreu, L.F. Vega, Modeling the solubility behavior of CO₂, H₂, and Xe in [C_n-mim][Tf₂N] ionic liquids, J. Phys. Chem. B 112 (2008) 15398–15406, <https://doi.org/10.1021/jp807484g>.
- [36] L.F. Vega, O. Vilaseca, F. Llovel, J.S. Andreu, Modeling ionic liquids and the solubility of gases in them: recent advances and perspectives, Fluid Phase Equil. 294 (2010) 15–30, <https://doi.org/10.1016/j.fluid.2010.02.006>.
- [37] J.O. Lloret, L.F. Vega, F. Llovel, Accurate description of thermophysical properties of Tetraalkylammonium Chloride Deep Eutectic Solvents with the soft-SAFT equation of state, Fluid Phase Equil. 448 (2017) 81–93, <https://doi.org/10.1016/j.fluid.2017.04.013>.
- [38] R.M. Ojeda, F. Llovel, Soft-SAFT transferable molecular models for the description of gas solubility in eutectic ammonium salt-based solvents, J. Chem. Eng. Data (2018), <https://doi.org/10.1021/acs.jced.7b01103>.
- [39] E.A. Crespo, L. Silva, J.O. Lloret, P.J. Carvalho, L.F. Vega, F. Llovel, J.A.P. Coutinho, A methodology to parameterize SAFT-type equations of state for solid precursors of deep eutectic solvents: the example of cholinium chloride, Phys. Chem. Chem. Phys. Just accep. (2019), <https://doi.org/10.1039/C9CP02548K>.
- [40] O. Vilaseca, F. Llovel, J. Yustos, R.M. Marcos, L.F. Vega, Phase equilibria, surface tensions and heat capacities of hydrofluorocarbons and their mixtures including the critical region, J. Supercrit. Fluids 55 (2010) 755–768, <https://doi.org/10.1016/j.supflu.2010.10.015>.
- [41] L.F. Vega, F. Llovel, F.J. Blas, Capturing the solubility minima of n-alkanes in water by soft-SAFT, J. Phys. Chem. B 113 (2009) 7621–7630, <https://doi.org/10.1021/jp9018876>.
- [42] J.K. Johnson, J.A. Zollweg, K.E. Gubbins, The Lennard-Jones equation of state revisited, Mol. Phys. 78 (1993) 591–618, <https://doi.org/10.1080/00268979300100411>.
- [43] J.C. Pàmies, L.F. Vega, Vapor-Liquid equilibria and critical behavior of heavy n-alkanes using transferable parameters from the soft-SAFT equation of state, Ind. Eng. Chem. Res. 40 (2001) 2532–2543, <https://doi.org/10.1021/>

- ie000944x.
- [44] E.A. Crespo, J.A.P. Coutinho, A statistical associating fluid theory perspective of the modeling of compounds containing ethylene oxide groups, *Ind. Eng. Chem. Res.* 58 (2019) 3562–3582, <https://doi.org/10.1021/acs.iecr.9b00273>.
- [45] F. Llovel, L.F. Vega, Global fluid phase equilibria and critical phenomena of selected mixtures using the crossover soft-SAFT equation, *J. Phys. Chem. B* 110 (2006) 1350–1362, <https://doi.org/10.1021/jp0551465>.
- [46] A.J. de Villiers, C.E. Schwarz, A.J. Burger, New association scheme for 1-alcohols in alcohol/water mixtures with sPC-SAFT: the 2C association scheme, *Ind. Eng. Chem. Res.* 50 (2011) 8711–8725, <https://doi.org/10.1021/ie200521k>.
- [47] F. Kruger, G.M. Kontogeorgis, N. von Solms, New association schemes for mono-ethylene glycol: cubic-Plus-Association parameterization and uncertainty analysis, *Fluid Phase Equil.* 458 (2018) 211–233, <https://doi.org/10.1016/j.fluid.2017.11.026>.
- [48] S.H. Huang, M. Radosz, Equation of state for small, large, polydisperse and associating molecules, *Ind. Eng. Chem. Res.* 29 (1990) 2284–2294, <https://doi.org/10.1021/ie00107a014>.
- [49] S.H. Huang, M. Radosz, Equation of state for small, large, polydisperse, and associating molecules: extension to fluid mixtures, *Ind. Eng. Chem. Res.* 30 (1991) 1994–2005, <https://doi.org/10.1021/ie00056a050>.
- [50] W. Dominik, J. Wojciechowska, On some properties of aqueous solutions of glycol monoethyl ether, *Przem. Chem.* 23 (1939) 61–65.
- [51] I.A. Bubnova, V.S. Timofeev, D.N. Chaplits, S.V. Lvov, L.L. Karpacheva, Phase equilibrium of binary systems formed by components of the hydraton of isobutylene, *Promst. Sint. Kauch.* 8 (1973) 1–3.
- [52] O.Y. Sartakova, M.S. Khristenko, Y.N. Garber, Phase equilibria in a multicomponent mixture for production of SKD-SR synthetic rubber, *Zh. Prikl. Khim.* 65 (1992) 1856–1863.
- [53] N.R. Nannan, C.M. De Servi, T. van der Stelt, P. Colonna, A. Bardow, An equation of state based on PC-SAFT for physical solvents composed of polyethylene glycol dimethylethers, *Ind. Eng. Chem. Res.* 52 (2013) 18401–18412, <https://doi.org/10.1021/ie401456q>.