

Measurement and Modeling of Isobaric Vapor–Liquid Equilibrium of Water + Glycols

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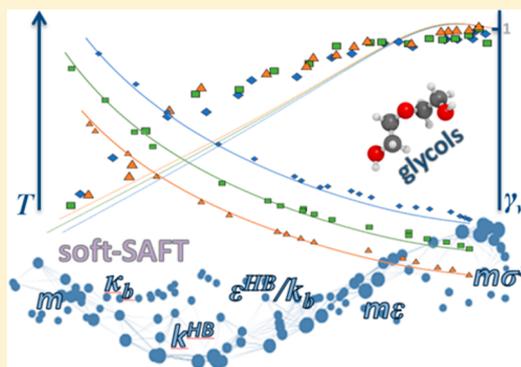
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Supporting Information

ABSTRACT: We present new experimental data on the isobaric vapor–liquid equilibria (VLE) of four binary mixtures of water with ethylene glycol, diethylene glycol, triethylene glycol, or tetraethylene glycol, measured at three different system pressures (0.05, 0.07, and 0.1 MPa). Water activity coefficients were estimated from the mixtures boiling temperatures and used to rationalize the effect of the increasing glycols chain length on the molecular interactions with water. The soft statistical associating fluid theory (SAFT) equation of state was used to describe the experimental VLE data of these highly nonideal systems, providing insights into the molecular interactions leading the macroscopic behavior of the mixtures. Glycols and water were both modeled as associating molecules, with models and parameters from previous works, in a transferable manner. Soft-SAFT accurately reproduces the experimental data using one single, state independent, binary interaction parameter to correct the mixtures dispersive energy. It is further shown that the parametrization obtained from the pure glycols can be used to provide accurate predictions of the water activities in aqueous solutions of PEGs of higher molecular weight (600–6000 g/mol) highlighting the soft-SAFT robustness and the soundness of the parametrization used.



INTRODUCTION

Glycols are organic compounds used in a large number of industrial applications as raw material due to their properties, like high boiling points, hygroscopicity, noncorrosiveness, and freezing-point depression. The glycols hydroxyl end groups make them popular intermediates in a large number of reactions, such as esterification, while low molecular weight glycols are commonly used in fibers treatment, paper, adhesives, printing inks, leather processes and natural gas processing, as dehydration agents, or precursors for polyester fibers and resins, polyurethanes, polyethylene terephthalate plastics, plasticizers, and coolants.¹

The physical properties and equilibrium data of glycols are extremely important in industry for the development of new technologies and the enhancement/optimization of existent processes. Moreover, the development of new technologies and the demand for new products impel the industry to continuously optimize existing processes, often relying on process simulators that, in turn, require correlations and/or thermodynamic models able to provide an accurate description of the system's thermodynamic behavior. However, due to their semiempirical character, the development of robust activity coefficient models and/or equations of state (EoS) is usually

dependent on the availability of experimental data, often scarce and of questionable accuracy.

The soft-SAFT (Statistical Associating Fluid Theory) ability to consistently describe the phase equilibrium and thermo-physical properties of a large number of compounds, using transferable molecular parameters derived from the pure compounds properties, have turned it into one of the most reliable thermodynamic models for the description of polar and associative compounds^{2,3} over a wide range of pressures and temperatures.^{4–6} The soft statistical associating fluid theory (SAFT) equation of state (EoS), as any molecular-based EoS, relies on the selection of a sound coarse-grained model capable of representing the basic physical features of the compounds. Soft-SAFT has been successfully applied to several experimental associating systems, including aqueous solutions, in excellent agreement with experimental data.⁷

We have recently proposed a simplified molecular model within the context of soft-SAFT to describe the glycols behavior

Special Issue: Emerging Investigators

Received: October 31, 2017

Accepted: February 20, 2018

Published: February 28, 2018

at high pressures, providing an excellent agreement with experimental data.⁵ The current work builds on it. Aiming at bridging the experimental gap, at or near atmospheric pressure, and evaluating the transferability of the previously proposed soft-SAFT models to mixtures, we present here a systematic study on the isobaric vapor–liquid equilibrium of four binary mixtures of water with ethylene glycol, diethylene glycol, triethylene glycol, and tetraethylene glycol at three different system pressures (0.05, 0.07, and 0.1 MPa). Additionally, the predictive capabilities of the soft-SAFT EoS are further evaluated by comparing experimental and modeled water activities in selected high molecular weight glycols, specifically PEG 400/600/1500/6000.

EXPERIMENTAL SECTION AND MODELING

Materials. Ethylene glycol (EG) was acquired from Fluka and the diethylene glycol (DEG), triethylene glycol (TriEG), and tetraethylene glycol (TeEG) were obtained from Sigma-Aldrich, with mass fraction purities higher than 99%. The water used was double distilled and deionized, passed through a reverse osmosis system and further treated with a Milli-Q plus 185 water purification equipment.

To remove traces of water, individual samples of each glycol were dried using 3 Å molecular sieves. The water content of the compounds was determined with a Metrohm 831 Karl Fischer coulometer (using the Hydranal–Coulomat AG from Riedel-de Haëns as analyte) and found to be lower than 30 ppm. The purity of each glycol was checked by ¹H and ¹³C NMR.

The full name, chemical structure, CAS number, molecular weight, average water content, mass purity, and supplier of each glycol are reported in Table 1.

Table 1. Chemical Structure, Compound Description, CAS Number, Molecular Weight, and Supplier of the Studied Glycols

Compound	Chemical structure
Ethylene glycol (EG) (CAS: 107-21-1; <i>M_w</i> = 62.07 g mol ⁻¹ ; <i>w_f</i> % = 99.5%; <i>w_{H2O}</i> <30 ppm) acquired from Fluka	
Diethylene glycol (DEG) (CAS: 111-46-6; <i>M_w</i> = 106.12 g mol ⁻¹ ; <i>w_f</i> % = 99%; <i>w_{H2O}</i> <30 ppm) acquired from Sigma Aldrich	
Triethylene glycol (TriEG) (CAS: 112-27-6; <i>M_w</i> = 150.17 g mol ⁻¹ ; <i>w_f</i> % = 99%; <i>w_{H2O}</i> <30 ppm) acquired from Sigma Aldrich	
Tetraethylene glycol (TeEG) (CAS: 112-60-7; <i>M_w</i> = 194.23 g mol ⁻¹ ; <i>w_f</i> % = 99%; <i>w_{H2O}</i> <30 ppm) acquired from Sigma Aldrich	

Vapor–Liquid Equilibrium. The VLE of the binary systems under study was determined at (0.1, 0.07, and 0.05) MPa using an isobaric microbullimeter developed and optimized in our group; the equipment description can be found in detail in previous publications.^{8,9} The liquid phase temperature was measured with a type K thermocouple, with a standard uncertainty of 0.05 K. The temperature probe was calibrated prior to the measurements by comparison with a NIST-certified Fluke calibration 1521 thermometer, with an uncertainty of 5×10^{-3} K. The internal system pressure was monitored and kept constant through a Buchi vacuum pump (model V-700) and a Buchi pressure controller unit (model V-850). The pressure was measured using a MKS Baratron type capacitance manometer (model 728A) kept at 100 °C and with an accuracy of 0.5%. The equilibrium was assumed to be reached when the temperature was constant (temperature drift lower than ± 0.05 K min⁻¹) for at least 5 min. The adequacy of the apparatus and methodology adopted to measure this type of

systems was previously established.^{8,9} The liquid phase composition was determined through an Anton Paar Abbemat 500 refractometer, with an uncertainty of 2×10^{-5} nD. Standards with compositions with an uncertainty of 1×10^{-5} g were used to determine a calibration curve that, through error propagation, was able to allow the determination of the sample composition within ± 0.001 mole fraction.

Soft-SAFT EoS. The prediction and/or correlation of phase equilibria and thermodynamic properties, using equations of state (EoS), remains highly relevant in chemical engineering due to an increasing demand for thermodynamic models suitable for a wide range of complex and macromolecular compounds. Clearly, the most apparent progresses toward such capabilities were accomplished through the development of molecular based EoSs based on statistical mechanics, which are able to explicitly account for different effects of molecular structure and interactions on the thermodynamic behavior.

A concept of such EoS was first proposed by Chapman and co-workers in the late 80s,^{10–13} based on the first-order thermodynamics perturbation theory of Wertheim,^{14–17} named SAFT (Statistical Associating Fluid Theory). In this theory, a (hard-sphere) reference fluid is perturbed by different contributions corresponding to different molecular effects (size, association, charges, etc.). Most SAFT-type equations such as soft-SAFT represent molecules as homonuclear chains composed of identical spherical segments. The equations are expressed in terms of the residual Helmholtz energy (A^{res}), which is expressed as a sum of different terms according to eq 1: a reference term (A^{ref}), accounting for the interactions between the different monomers (segments or spheres), a chain formation term (A^{chain}) and a contribution from the strong, short-range and highly directional associative forces such as hydrogen bonding (A^{assoc}). Additional terms can be added, for instance, polar terms, depending on the specific interactions.

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

Soft-SAFT,^{2,3} uses a Lennard-Jones (LJ) reference fluid, considering both the repulsive and attractive interactions in a single contribution as described in the work of Johnson et al.¹⁸ Thus, the reference term defines the monomer using two different parameters: the segment diameter, σ , and the energy of interaction between segments, ϵ/k_B . These two parameters, along with the number of segments (related to the chain length), m , are the three nonassociating pure-component parameters in the soft-SAFT EoS. The LJ contribution can be extended to mixtures under the van der Waals one-fluid theory, with the generalized Lorentz–Berthelot (LB) combining rules for the unlike size and energy parameters:

$$\sigma_{ij} = \eta_{ij} \left(\frac{\sigma_i + \sigma_j}{2} \right) \quad (2)$$

$$\epsilon_{ij} = \xi_{ij} \sqrt{\epsilon_i \epsilon_j} \quad (3)$$

In eqs 2 and 3, η_{ij} and ξ_{ij} are the size and energy binary parameters that become one when using a predictive approach. When dealing with associating components, the A^{assoc} contribution is enabled, requiring two additional molecular parameters related to the energy (ϵ^{HB}/k_B) and volume (κ^{HB}). These parameters are related to the energy and volume of square-well sites located embedded off-center the LJ segments, mimicking the association phenomenon.² The number of sites as well as the values of the parameters depend on the systems

under investigation and should be specified as part of the proposed molecular model for the system. The cross-association parameters are usually obtained from the pure-component parameters using the following combining rules:

$$\varepsilon_{ij}^{\text{HB}} = \sqrt{\varepsilon_{ii}^{\text{HB}} \varepsilon_{jj}^{\text{HB}}} \quad (4)$$

$$\kappa_{ij}^{\text{HB}} = \left(\frac{\sqrt[3]{\kappa_{ii}^{\text{HB}}} + \sqrt[3]{\kappa_{jj}^{\text{HB}}}}{2} \right)^3 \quad (5)$$

although some other combinations are also possible.

The vapor–liquid equilibria between the two phases, L and V , require the equality of temperature, pressure, and chemical potentials of the different species in both phases. In the framework of soft-SAFT, both the chemical potentials and pressure are obtained as a function of temperature, composition, and density, and thus the equilibrium conditions are²

$$p^L(\rho^L, z^L, T) - p^V(\rho^V, z^V, T) = 0 \quad (6)$$

$$\mu_i^L(\rho^L, z^L, T) - \mu_i^V(\rho^V, z^V, T) = 0; \quad i = 1: \text{NC} \quad (7)$$

where p , μ_i , T , ρ , z and NC are the pressure, chemical potential of specie i , temperature, density, composition and number of components.

Provided initial guesses of the two coexistence densities, a nonlinear solver is used in the soft-SAFT code to find the solution of the system of equations (i.e., eqs 6 and 7) allowing to obtain the vapor pressure for a given temperature and composition. Alternatively, using the Gibbs phase rule, is possible to specify a priori the composition in one phase or pressure and solve the system of equations.

Molecular Model. To apply SAFT to experimental systems, a molecular model for each compound should be proposed, able to represent the basic physical features of the different compounds. In recent publications,^{5,6} a molecular model for polyethers was proposed within the framework of soft-SAFT EoS and compared to experimental data. The model was able to accurately describe the VLE, $p\rho T$, and second-order derivative properties of these systems. Glycols were modeled as homonuclear chainlike molecules; each hydroxyl end-group was mimicked by a square-well association site (type A), two per molecule, embedded off-center in one of the segments forming the chain, with AA interactions being allowed for the pure fluid. Moreover, by representing the hydroxyl group as one single association site, the different associative interactions within the functional group are not discriminated as it is the case for more detailed models as those used for alkan-1-ols¹⁹ and water.²⁰ Instead, a dual nature of the association site mimicking the whole functional group is considered. Additionally, the effects due to the lone pair of electrons in each oxygen of the ethylene oxide groups is implicitly accounted for through the parameters. This is clearly a simplification of the model, which facilitates the transferability of the molecular parameters to high molecular weight glycols, in particular mixtures of polyols. The molecular parameters for the glycols, studied in this work, were directly transferred from our previous work⁵ and are presented in Table 2.

Water was modeled following the work of Vega et al.²⁰ with a 4-site associating model,²¹ two sites (B) representing the hydrogen atoms and two association sites (C) representing the

Table 2. Soft-SAFT Molecular Parameters for the Compounds Studied in This Work Modeled as Homonuclear Chainlike Molecules with AA Interactions Allowed for the Pure Fluid^{5,20}

	m	σ (Å)	ε/k_B (K)	$\varepsilon^{\text{HB}}/k_B$ (K)	κ^{HB} (Å ³)
EG	1.951	3.533	325.10	4140	2600
DEG	2.825	3.733	342.77	3891	2600
TriEG	3.525	3.887	346.18	3891	2600
TeEG	4.311	3.964	349.14	3891	2600
PEG 400 ^a	8.321	4.049	357.47	3891	2600
PEG 600 ^a	12.110	4.090	360.20	3891	2600
PEG 1500 ^a	29.156	4.141	363.76	3891	2600
PEG 6000 ^a	114.386	4.168	365.649	3891	2600
water	1.000	3.154	365.00	2388	2932

^aParameters extrapolated from the correlations proposed by Crespo et al.⁵ [$m = 0.01894M_w + 0.7461$; $m\sigma^3 = 1.38015M_w + 0.26992$; $m\varepsilon/k_B = 6.93761M_w + 199.509$].

lone pairs of electrons in the oxygen with BC interactions being allowed in pure water. The water molecular parameters are reported in Table 2. In the case of the water + glycol mixtures, cross-association interactions between water and glycol molecules are also considered, and the corresponding association strength is obtained in a fully predictive manner through eqs 4 and 5.

RESULTS AND DISCUSSION

Experimental isobaric VLE data for binary systems of water with the selected glycols were measured at (0.1, 0.07 and 0.05) MPa, glycols mole fractions up to 0.8 and temperatures up to 430 K, as depicted in Figure 1 and reported in Tables S1 through S4 (in Supporting Information).

Ethylene glycol + water binary system is the most widely studied mixture. However, most of those works report equilibrium data at pressures lower than those investigated here. For instance, vapor–liquid equilibria data at or near 0.1, 0.07, or 0.05 MPa were reported by Trimble and Potts,²² Kireev and Popov,²³ Lancia et al.,²⁴ Kamihama et al.²⁵ and others, whose data are not easily accessible. As depicted in Figure 2. Large discrepancies are observed among the different sources; data reported back in the decade of 1930 by Trimble and Potts²² and Kireev and Popov²³ present high discrepancies toward that published by Lancia et al.,²⁴ Kamihama et al.²⁵ and ours. In fact, data reported here and that reported by Kamihama et al.²⁵ are in excellent agreement, with %AAD of 0.94%. The data reported by Lancia et al.,²⁴ for pressures that range from 0.09 to 0.12 MPa, present also a good agreement, with small deviations related to the differences in the system pressure.

Diethylene glycol + water vapor–liquid equilibrium data is also available in the literature, but as for EG much of the data is of difficult access. Jelinek et al.²⁶ reported data for DEG + H₂O binary system, for 0.099 MPa, that presents large discrepancies toward that reported here, as depicted in Figure 2. Triethylene glycol + water vapor–liquid equilibrium data were reported by Mostafazedh et al.²⁷ at 0.085 MPa, with the data presenting a similar behavior to that reported here for the glycol mole fractions up to 0.4. For higher mole fractions the behavior starts to deviate with boiling temperatures reported by the authors being lower than those measured here.

Tetraethylene glycol + water binary system, at pressures close to those reported here, were reported by Yu et al.²⁸ with our

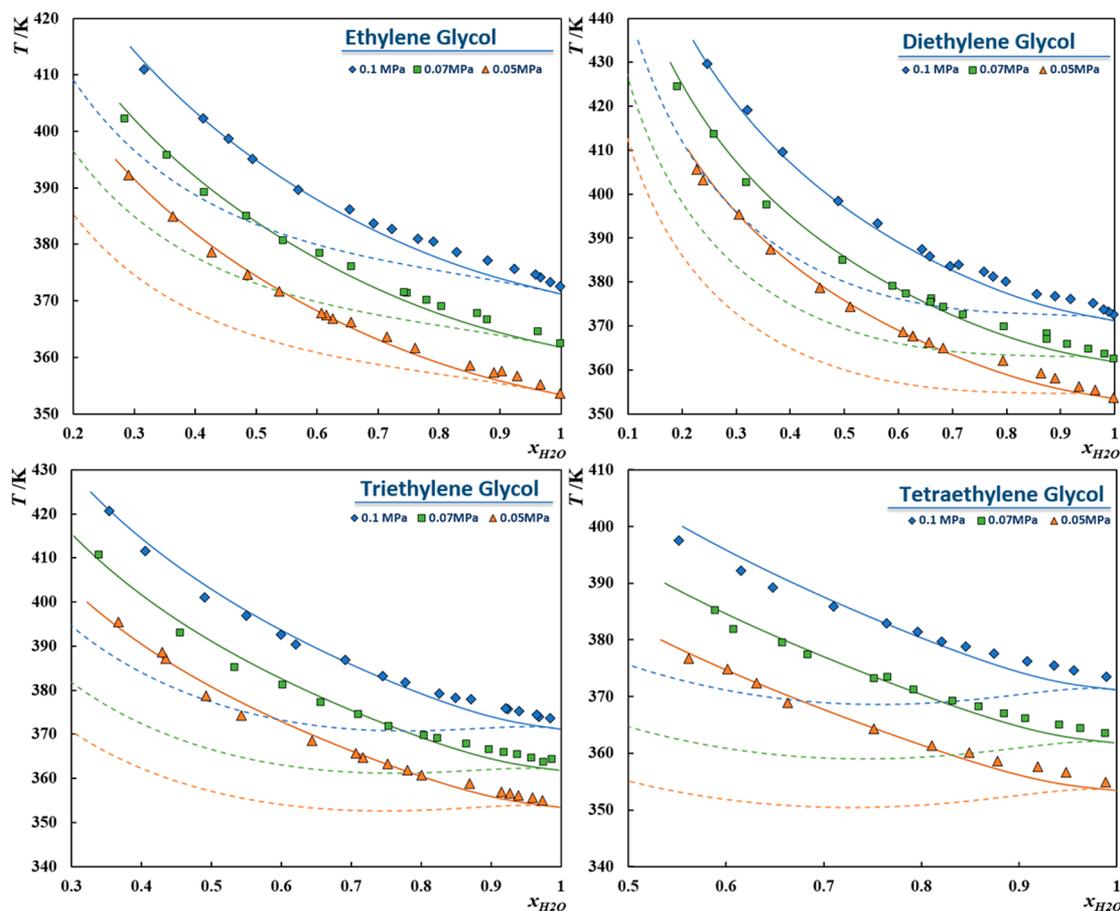


Figure 1. Isobaric temperature–composition diagram of the glycols + H₂O binary systems. The dashed and solid lines represent the soft-SAFT EoS predictions and fitting, with one binary parameter, to the experimental data, respectively.

results in excellent agreement with the ones reported by these authors with an %AAD of 0.19%.

We present in Figure 1, a comparison between soft-SAFT calculations as predicted from pure component parameters (dashed lines in the figure), observing a systematic underprediction of the mixtures boiling temperatures. On the contrary, very good agreement with the experimental data is attained with one single, pressure independent binary interaction parameter, correcting the mixtures dispersive energy (eq 3). This allowed the soft-SAFT to describe the experimental data of the different systems, with a %AAD of 3.82%. Binary interaction parameters, greater than unity, reported in Table 3, were necessary for all the systems, suggesting that the model underestimates the magnitude of the interactions between glycols and water as well as the glycols chain length effect. This is also in agreement with the increase in the mixtures boiling temperature with the glycols chain length, due to an increase of the van der Waals dispersion forces. Notice, however that some deviations are observed as the mole fraction of water is increased, for all cases.

The water activity coefficients (γ_w) estimated from the mixtures boiling temperatures can be used to evaluate the nonideality of aqueous systems, using the generalized modified Raoult's law, expressed by

$$\gamma_w = \frac{y_w \phi_w^V p}{x_w \phi_w^* p^*} \quad (8)$$

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

As the pressures investigated in this work are low, the fugacity coefficients are close to unity. Furthermore, due to the glycols low volatility (soft-SAFT results show glycols mole fractions, in the vapor phase, always lower than 10%) the system vapor phase can be considered composed entirely by water, allowing eq 8 to be simplified as

$$\gamma_w = \frac{p}{x_w p_w^*} \quad (9)$$

The water activity coefficients estimated from the mixtures' boiling temperatures and predicted with soft-SAFT EoS are depicted in Figure 3. As can be observed, a good agreement between experimental data and model results is found considering the simplifications made in the estimation of the activity coefficients. The high deviations observed for ethylene glycol are most probably due to the oversimplifications of the model used for the estimation of the activity coefficients from the experimental data, as ethylene glycol presents a considerably higher volatility than its homologues, and consequently, the vapor phase is richer in this compound than for the rest of the series. An additional explanation is that the water–EG hydrogen-bonding interactions, which are dominant, given the short length of the EG, are not well

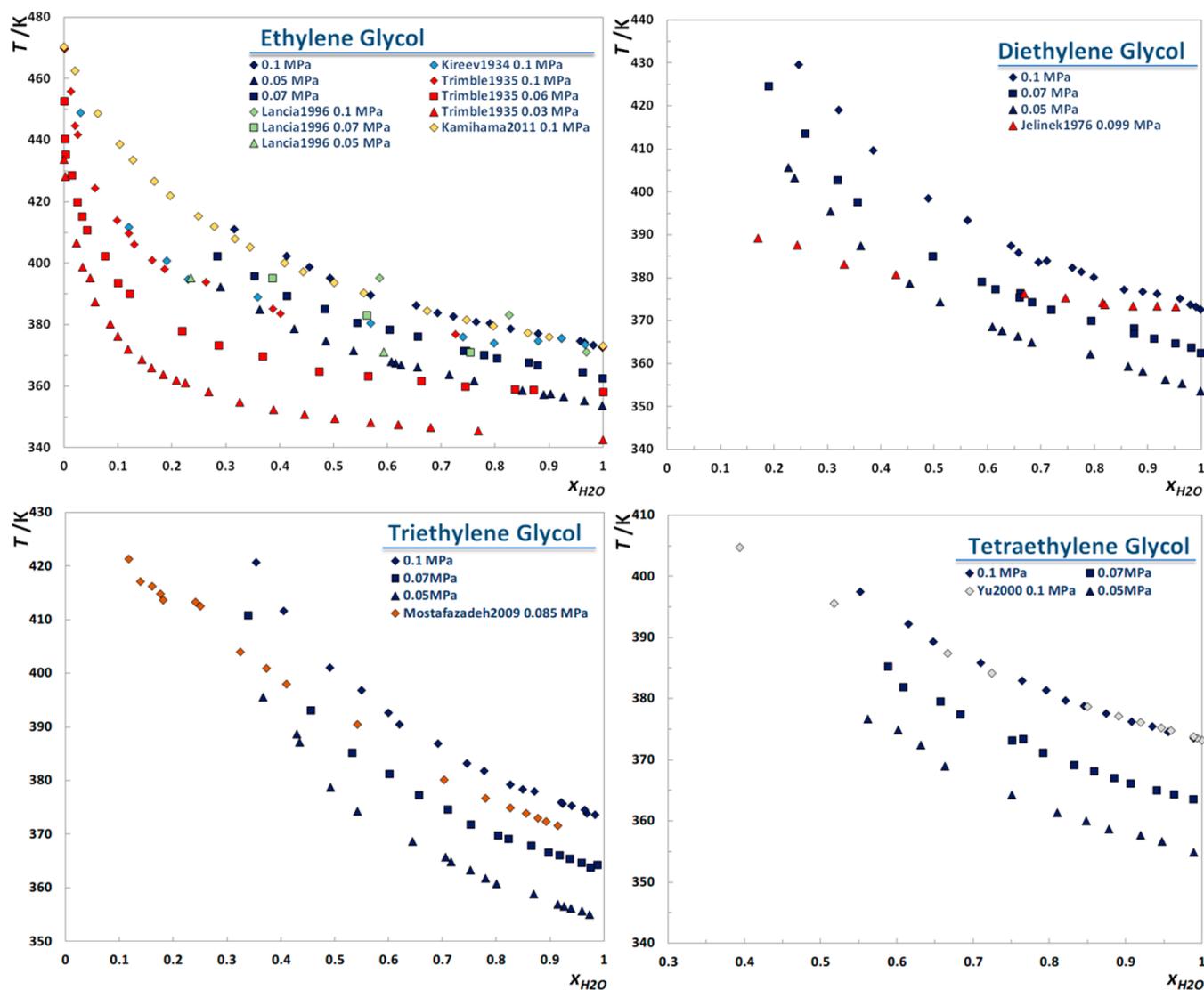


Figure 2. Isobaric temperature–composition diagram of the glycols + H₂O binary systems of the experimental and literature data.^{22–28}

Table 3. Binary Interaction Parameters and Modeling Results for the Systems Studied in This Work

	ξ_{ij}	%AAD (x)	%AAD (γ)
EG + water	1.130	3.87	5.49
DEG + water	1.135	4.33	5.63
TriEG + water	1.175	3.93	5.74
TeEG + water	1.185	3.14	5.09

described by the simplified model, as the OH group is represented only by one associating site. The assumptions in the estimations and the molecular model seem to be good for the rest of the mixtures, as the glycols increase their molecular weight. Also, as shown in Figure 3, the systems studied present water activity coefficients very close to unity for low concentrations of glycol where the water–water interactions dominate.

Furthermore, as the glycols chain length increases, soft-SAFT predicts the existence of a maximum on the water activity coefficients (values very close to 1) denoting a region in which unfavorable interactions dominate the system. This suggests that as the size of the glycol molecules increase, their interactions with water decrease in the full solvation regime.

It is also observed that for higher mole fractions of glycol there is a regular decrease of the water activity coefficients, denoting the existence of favorable intermolecular interactions between the two species; contrarily to what is observed in the solvation regime, it increases with increasing glycols chain length. This is nevertheless, translated into values of the binary interaction parameters applied within soft-SAFT that also increase following the same trend. It is important to remark that the mixtures behavior has been corrected just with one binary parameter for the van der Waals interactions, while the cross-association, hydrogen-bonding interactions, were always calculated from eqs 4 and 5, in a predictive manner.

One of the advantages of using molecular-based EoSs is the physical meaning of their parameters. As a consequence, the nonassociative pure-component parameters for a homologous series are usually correlated with the compounds molecular weight while the association parameters are often kept constant after the first or second member of the series.^{3,5,6,29,30} This allows the prediction of the molecular parameters for compounds not included in the fitting procedure, and for which little or no pure-component data are available for parametrization, as it is the case for longer polyethylene glycols.

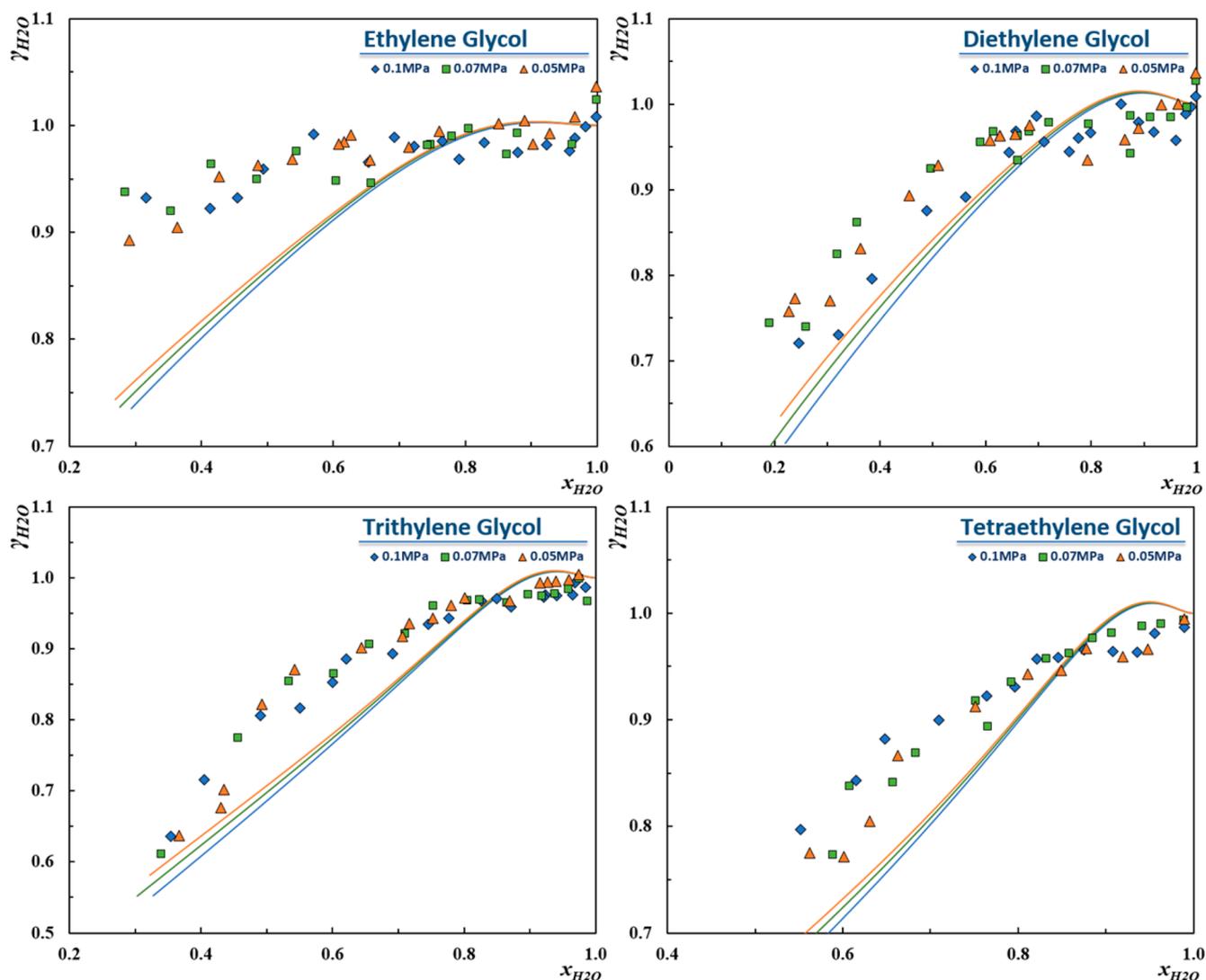


Figure 3. Water activity coefficients for the binary systems of water + glycols at 0.1, 0.07, and 0.05 MPa. The solid lines represent the soft-SAFT EoS calculations and the symbols represent estimations from the experimental boiling temperatures.

Therefore, as the transferability of the glycols parameters to higher chain length PEG's was previously shown,⁵ the correlations proposed in that work were here applied to obtain the soft-SAFT parameters for the various PEGs listed in Table 2 in an attempt to further demonstrate the robustness of soft-SAFT EoS to investigate the VLE of PEGs + water binary systems.

Ninni et al.³¹ reported water activities in poly(ethylene glycol) aqueous solutions at 298 K for PEG molecular weights ranging between 200 and 20000 g/mol while Herskowitz and Gottlieb³² reported experimental water activities in PEG (200–6000 g/mol) solutions in the 293.1–333.1 K temperature range. However, most of this data are limited to very high mole fractions of water providing little insights into the overall systems behavior. Thus, only selected data for PEG 400, PEG 600, PEG 1500, and PEG 6000 over a broader concentration range were modeled using soft-SAFT EoS.

As depicted in Figure 4, a binary interaction parameter $\xi = 1.220$ was found to provide a good description of the water activities in a PEG 400 aqueous solution. As this parameter corrects the van der Waals energy parameter (ϵ/κ_B), it is expected that increasing the glycols chain length, ξ , should

result in an asymptotic behavior as the magnitude of the interactions between the two components becomes independent of the glycols chain length. Therefore, the binary interaction parameter fitted to the binary system PEG 400 + water was used to model the water activities in aqueous solutions of PEG 600/1500/6000 at different temperatures and, as depicted in Figure 4, a very good description of the experimental data was achieved.

The good results obtained for PEG 600, 1500, and 6000 are particularly remarkable as they represent full predictions of the model with the PEG pure-component parameters being obtained from the correlations proposed in our previous work and the binary interaction parameter transferred from PEG 400. Moreover, as explained in the modeling section, a simplified molecular model is being used to describe the PEG molecules where the hydrogen-bonding character of each of the hydroxyl end-groups is mimicked through one association site and the influence of the high number of ethylene oxide groups is being accounted implicitly by the specific values of the nonassociative parameters. An additional simplification is related to the polymer's molecular mass distribution as these polymers are mixtures of PEG's with different molecular

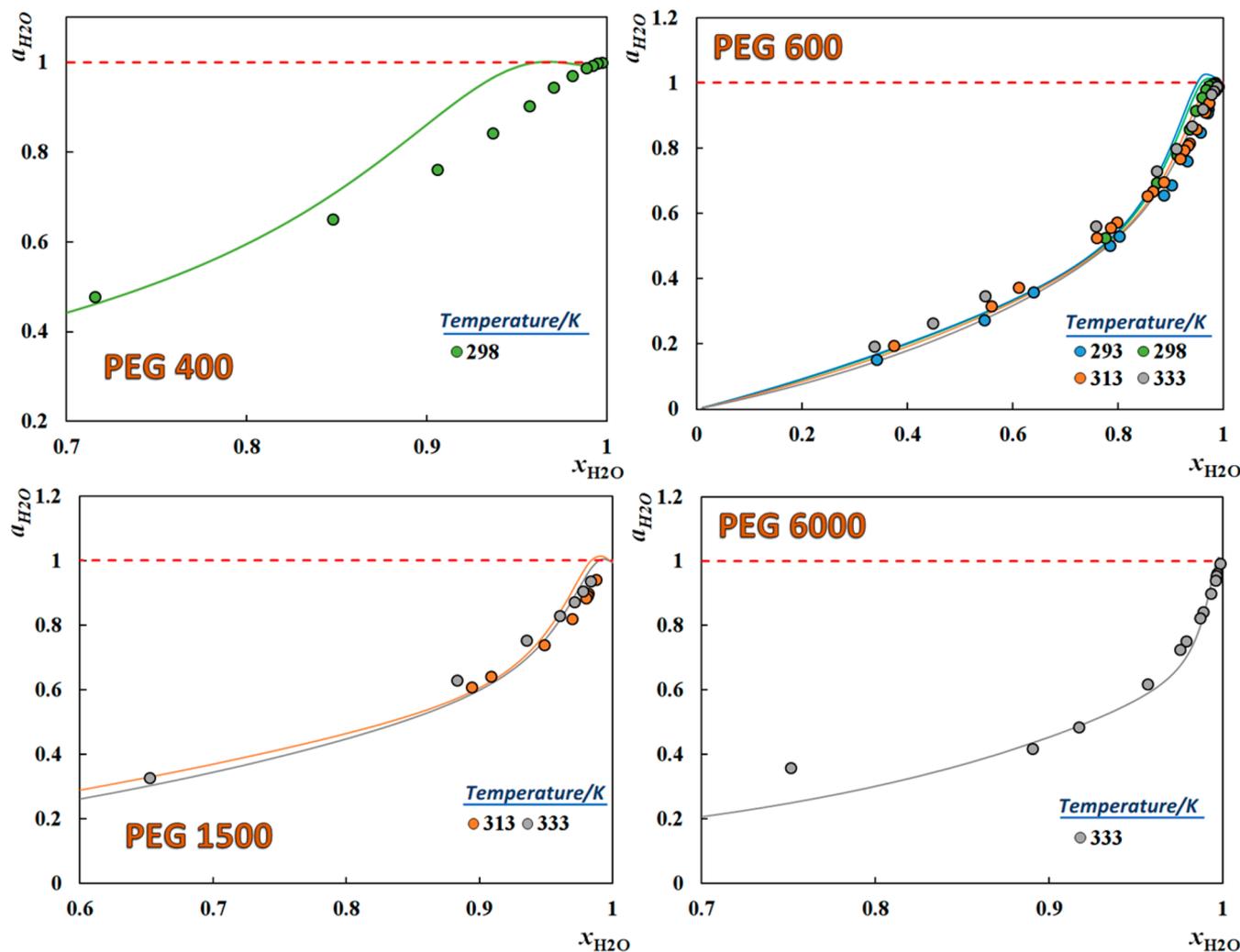


Figure 4. Water activity for the binary systems water + PEGs.^{31,32} The solid lines represent the soft-SAFT predictions.

weights, which are in soft-SAFT considered by a pseudopure component approach. This seems to be particularly important in PEG 400, where the water activities calculated with soft-SAFT are for water-rich solutions higher than those observed experimentally, suggesting that the distribution of the PEG 400 may be actually displaced toward higher values.

Additionally, as observed both experimentally and with the modeling, for PEG 600 and PEG 1500 temperature plays a minor role on the magnitude of the interactions between the two components with soft-SAFT predicting a decrease on the water activities as the temperature increases.

CONCLUSIONS

A systematic experimental study on the isobaric vapor–liquid equilibrium of four binary mixtures of water with ethylene glycol, diethylene glycol, triethylene glycol, and tetraethylene glycol at three different system pressures (0.05, 0.07, and 0.1 MPa) is here reported overcoming the lack of experimental data available in the literature at or near atmospheric pressure.

The soft-SAFT EoS was applied to describe the phase equilibria of the studied systems and good results were obtained using one single pressure independent binary interaction parameter. This binary parameter was found to be greater than one for all the studied systems denoting the systematic underestimation of the interactions between glycols

and water, that slightly increase with the glycols chain length increase. Furthermore, soft-SAFT provides a fair description of the estimated water activity coefficients of the studied systems. Deviations between soft-SAFT and the estimated values may be partially due to the simplifications used to obtain the estimations. Although in the solvation regime activity coefficients close to 1 are observed, when the glycols mole fraction increases a regular decrease of the water activity coefficients is observed, evidencing the presence of favorable interactions between the water and the glycol, due to hydrogen bonding forces, well captured by soft-SAFT.

Taking advantage of the transferability of soft-SAFT parameters, accurate predictions of the water activities in aqueous solutions of high molecular weight PEG's (600–6000 g/mol) were achieved, using pure-component parameters obtained from correlations and a binary interaction parameter transferred from PEG 400. This confirms the robustness of the model and the transferability of the molecular parameters to members of the series not included in the fitting procedure.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jced.7b00945.

Experimental VLE data and activity coefficients; refractive indexes (PDF)

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Funding

This work was supported by Partex Oil and Gas and was developed in the scope of the project CICECO—Aveiro Institute of Materials, POCI-01-0145-FEDER-007679 (ref. FCT UID/CTM/50011/2013), financed by national funds through the FCT/MEC and cofinanced by FEDER under the PT2020 Partnership Agreement. P. J. Carvalho acknowledges FCT for a contract under the Investigador FCT 2015, Contract No. IF/00758/2015. E. A. Crespo acknowledges FCT for the Ph.D. Grant SFRH/BD/130870/2017.

Notes

The authors declare no competing financial interest.

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