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## **Soft-SAFT Equation of State as a Valuable Tool for the Design of new CO<sub>2</sub> Capture Technologies.**

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### **Abstract**

The design, simulation and/or optimization of new processes rely on the availability of robust and accurate models or equations of state (EoS). However, traditional cubic equations of state (EoS's), traditionally used in many process simulators, fail on describing complex polar and associating behavior of some molecules, leading to unreliable results and hence, poor design and optimization. This problem can be overcome with the use of robust, reliable equations of state. This work belongs to a long term project assessing the performance and usefulness of an advanced EoS (soft-SAFT), as a valuable tool for the description of highly non-ideal systems and thus, for the reliable simulation/design of new technologies.

We focus here on assessing the validity of soft-SAFT, a molecular-based EoS, for the development of novel technologies for CO<sub>2</sub> capture using polyether blends as solvent. Within soft-SAFT polyether molecules are modeled as chains with end-groups having an association site, explicitly mimicking the hydroxyl end-groups. The study comprises polyethers, including glymes, and their mixtures with CO<sub>2</sub> at different conditions. It is shown that soft-SAFT is able to successfully describe the thermodynamic behavior (e.g. vapor pressures and liquid densities) of these solvents in wide temperature and pressure ranges. Moreover, by explicitly considering the quadrupolar moment of CO<sub>2</sub>, and using one, temperature and pressure independent binary interaction parameter, an accurate description of the gas solubilities in several polyethers was achieved. For glymes, which among polyethers exhibit the highest CO<sub>2</sub> solubilities, such parameter was found to correlate with the molecular weight of the solvent. Finally the equation was used to predict the thermal and pressure cycle capacities of the different solvents. Results presented here reinforce the use of soft-SAFT as a reliable tool for solvent screening, offering reliable predictions of phase equilibria and solubility behavior in a wider number of systems.

## Introduction

In average, up to two thirds of the crude oil remains trapped in the oil reservoirs after primary and secondary phases of oil recovery. (Gudina et al. 2012; Kuuskraa et al. 2013) Given the growing global energy demand and emergent oil reserves depletion, the development and optimization of enhanced oil recovery (EOR) technologies are of increasing importance. Carbon Capture and Sequestration (CCS) are a set of technologies for the separation of carbon dioxide (CO<sub>2</sub>) from different sources that can then, be injected deep underground for long-term storage and isolation. CO<sub>2</sub>-EOR has been suggested as a type of CCS technology that allows for both the production of additional oil and the decrease on greenhouse gases (GHG) emissions.(International Energy Agency (IEA) 2016) In CO<sub>2</sub>-EOR, CO<sub>2</sub> is captured at a nearby plant or other industrial facility, and transported by pipeline to oil fields, where it is compressed prior to its injection into the reservoir. Once in the reservoir, the CO<sub>2</sub> mixes with the oil, swelling it and making it lighter and less viscous which, along with the increased pressure in the reservoir, releases additional oil to a nearby production well.(Advanced Resources International 2006; Melzer 2012) CO<sub>2</sub>- EOR is thus, a promising alternative to the usual CCS technologies since the already explored oil and gas fields are able to retain most of the injected CO<sub>2</sub>, provided the integrity of the geological structures. In this way, in addition to the incoming revenues generated from the additional oil produced, oil fields provide well-characterized sites for CO<sub>2</sub> storage, allowing to partly offset the high cost of CO<sub>2</sub> capture.

Nevertheless, despite the fact that the oil and gas industry possesses the required know-how and recognizes the potential of this technology, at present CO<sub>2</sub>-EOR only contributes for about 0.35% of the global oil production as the ability to widely deploy such techniques has been hindered by the availability of suitable and economically viable supplies of CO<sub>2</sub>. (International Energy Agency (IEA) 2015) Hence, the development and optimization of new, cheaper and more efficient, separation processes for CO<sub>2</sub> capture remains a challenging task to the oil industry, closely tight to the fundamental understanding of the interactions CO<sub>2</sub>-solvent and, consequently, to an accurate description of the thermodynamic behavior of the solvents themselves.

Among the different processes for CO<sub>2</sub> capture, the oxygenation of alkyl chains is a well-known approach for enhancing the CO<sub>2</sub> solubilities, (Carvalho et al. 2016) being the basis of the two most successful industrial processes for natural gas sweetening (Rectisol (Engineering 2007) and Selexol (Breckenridge et al. 2000; LLC 2007)). For this reason several polyethers, including glycols, glymes and polymers have been attracting considerable attention as feasible candidates to CO<sub>2</sub> capture but, despite the industrial interest for these compounds, their thermophysical characterization was surprisingly poor. Trying to overcome these gap, aiming to fully characterized this family of compounds a series of studies have been done in the latest years by our groups (Carvalho et al. 2015; Crespo et al. 2017; Navarro et al. 2017). Nonetheless, the CO<sub>2</sub> sorption mechanism in these compounds is still unclear.

Although traditional and cubic EoS are still widely used in the chemical and oil industry, one of their main limitations is their inability to deal with complex polar (e.g. CO<sub>2</sub>) and associating molecules (e.g. glycols, glymes, water); hence, they are being progressively replaced by more advanced EoS where these molecular effects are taken into account. The development of new molecular models and/or EoS able to provide a physical interpretation of the system becomes necessary prior to the design, simulation, technical and economic analysis of new processes and configurations, through a chemical process simulator. Among the advanced equations used for these calculations, SAFT-type equations are becoming very popular, as they have proven to provide reliable results. These EoS are based on statistical mechanics, (Chapman et al. 1988; Huang and Radosz 1990) and the molecular structure is built into the equation, providing a framework in which the effects of molecular shape and different intermolecular interactions are explicitly considered and isolated from each other. This, along with the physical meaning of its parameters, and their versatility, allow these equations to become a standard for engineering design (Müller and Gubbins 2001; Paricaud et

al. 2002), with soft-SAFT staging as one of the most successful variants of the equation. (Blas and Vega 1997, 1998)

This work aims at assessing the performance of soft-SAFT for the description of the CO<sub>2</sub> solubilities in different polyethers in a wide range of temperatures and pressures, as a first step on investigating their performance for CO<sub>2</sub> capture. The experimental data, its subsequent modeling and inherent interpretation, at a molecular level, will allow to discuss the solvation mechanism, the feasibility of these polyethers as potential solvents for CCS technologies and to create heuristic rules for the design of task-specific compounds with enhanced CO<sub>2</sub> solubility.

## Methodology

### soft-SAFT Modelling

soft-SAFT (Blas and Vega 1997, 1998), as most SAFT-type equations, describes the residual Helmholtz energy of a system as the sum of different contributions accounting for different molecular effects. Thus, the residual Helmholtz energy of the system ( $A^{res}$  - Equation 1) is obtained as the sum of a reference term,  $A^{ref}$ , that accounts for both the attractive and repulsive forces between groups making the molecule (usually named segments or monomers), a contribution due to the chain formation,  $A^{chain}$ , a contribution due to the strong and highly directional forces (usually called associating forces),  $A^{assoc}$ , and a polar term,  $A^{polar}$ , that accounts for polar and multipolar interactions in molecules exhibiting a strong polar moment (dipole, quadrupole, etc.)

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

The different SAFT variants usually differ on the reference term, while using identical chain and association terms derived from Wertheim's theory. (Wertheim 1984a, b, 1986a, b) In soft-SAFT, the reference term is given by a Lennard Jones (LJ) spherical fluid that considers both repulsive and attractive interactions in a single contribution, as described by Johnson et al. (Johnson et al. 1993). This term defines the LJ reference fluid using two molecular parameters: the sphere (segment) diameter of the monomers or groups integrating the molecule,  $\sigma$  and the dispersive energy between segments,  $\varepsilon/k_B$ , that along with the chain length,  $m$ , from the chain term, fully describe a non-associating and non-polar molecule within soft-SAFT.

In order to extend the LJ contribution to mixtures, the van der Waals one-fluid theory is considered, with the unlike size and energy parameters obtained through the generalized Lorentz-Berthelot (LB) mixing rules:

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

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

In Equations 2–3,  $\eta_{ij}$  and  $\xi_{ij}$  are the size and energy binary adjustable parameters, respectively, these being equivalent to the  $(1 - E)$  and  $(1 - k)$  commonly applied in classical cubic EoS. It is important to clarify that, when both binary parameters are set to unity, the model becomes fully predictive. This means, the model can be used to calculate multicomponent mixtures without the need to fit any mixture data, in a purely predictive manner.

For associating molecules, two additional parameters are required, namely the energy ( $\varepsilon^{HB} / k_B$ ) and volume ( $K^{HB}$ ) of the association sites. Additionally, a proper association scheme specifying the number/type of association sites and allowed interactions has to be assigned to each associating compound in order to mimic the associating forces (i.e. hydrogen bonding and others) happening in the experimental systems.

The extension to mixtures of the association term requires the evaluation of the cross-association energy ( $\varepsilon_{ij}^{HB} / k_B$ ) and volume ( $\kappa_{ij}^{HB}$ ), for which the following mixing rules are usually considered:

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

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

The last term of Equation 1,  $A^{polar}$ , is a multipolar contribution that is considered when dealing with fluids exhibiting a polarity capable of significantly influence the physical interactions, as it is the case of the quadrupole in CO<sub>2</sub>. The implementation of this term includes an effective quadrupole moment,  $Q$ , and the fraction of segments in the chain that effectively contains the moment,  $x_p$ . Both parameters are related to the experimental multipolar moment by the following expression:

$$Q = Q_{exp} \cdot x_p \quad (6)$$

### Molecular Models

In molecular based EoS, the adequate selection of a coarse-grained model able to represent the physical features of the different compounds is of an outstanding relevance for the good performance of the equation. soft-SAFT was recently applied by us (Crespo et al. 2017; Navarro et al. 2017) to accurately describe the vapor-liquid equilibrium (VLE),  $ppT$  and second-order derivative properties of several glycols and glymes using a ‘simple’ but reliable molecular model. The model applied in those works considers the polyethers as LJ chains composed of equal-sized segments with associating sites embedded off-center mimicking each hydroxyl end group (i.e. two, one and zero for glycols, mono and di-alkyl glymes, respectively) while allowing for interactions between all the association sites. A schematic representation of the model is presented in Figure 1 for a generic glycol.

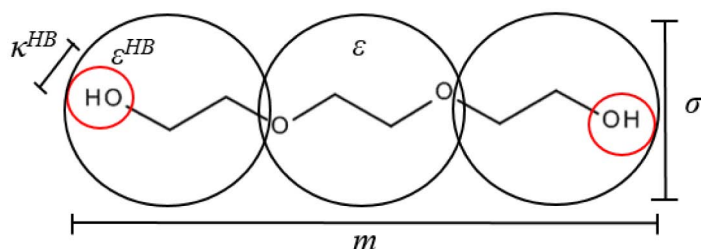


Figure 1—Sketch of the soft-SAFT molecular model for polyethers. The number of association sites (red circles) is equal to the number of hydroxyl end-groups.

Encouraged by the good results obtained using these simple models, the same approach is followed here with the molecular parameters for the different polyethers inherited from our previous works and reported in Table 1. One of the main advantages of soft-SAFT is its transferability; as a consequence, by studying a small number of members of a family of compounds, correlations of the molecular parameters based on the compounds molecular weight can be developed, allowing for the prediction of the thermodynamic behavior of other members not included in the fitting procedure and/or for high chain length members for which little to none experimental data is typically available. Such correlations were developed in our previous works and are here applied to describe the CO<sub>2</sub> solubilities in two of those compounds (e.g. TriEGME and PEGDME250).

CO<sub>2</sub> is modeled as a LJ chain in which polar interactions are explicitly considered. Consequently, in addition to the three non-associating molecular parameters,  $m$ ,  $\sigma$  and  $\varepsilon$ , two additional parameters are

required, namely the quadrupole moment,  $Q_{\text{exp}}$ , and the fraction of segments in the chain that contains the quadrupole,  $x_p$ . The  $\text{CO}_2$  parameters were directly taken from previous work (Pedrosa et al. 2005) and are also reported in Table 1.

In this work, a careful selection of a large set of polyethers to be analyzed was carried out, aiming at evaluating the impact of different structural effects, such as the molecules chain length (increase of the number of ether groups) or, the effect of replacing the hydrogen(s) of the glycols hydroxyl end group(s) by a methyl or ethyl group (which influences the hydrogen bonding character of the solvent) on the solvent properties and in their interactions with  $\text{CO}_2$ . The set of compounds includes: diethylene glycol (DEG), diethylene glycol methyl ether (DEGME), diethylene glycol ethyl ether (DEGEE), triethylene glycol methyl ether (TriEGME), tetraethylene glycol methyl ether (TeEGME), diethylene glycol dimethyl ether (DEGDME), triethylene glycol dimethyl ether (TriEGDME), tetraethylene glycol dimethyl ether (TeEGDME) and poly (ethylene glycol) dimethyl ether (PEGDME250,  $\bar{M}_n = 250 \text{ g} \cdot \text{mol}^{-1}$ ).

Table 1—soft-SAFT pure-component parameters used in this work.

Compound	$M_w$ (g/mol)	$m$	$\sigma$ (Å)	$\varepsilon/k_B$ (K)	$\varepsilon^{HB}/k_B$ (K)	$k^{HB}$ (Å)	$10^{40} Q_{\text{exp}}$ (C·m <sup>2</sup> )	$x^p$
DEGa	106.12	2.825	3.733	342.77	3891	2600		
DEGME <sup>b</sup>	120.15	2.995	3.889	330.50	3450	2600	-	-
DEGEE <sup>b</sup>	134.17	3.165	4.009	331.00	3450	2600	-	-
TriEGMEb*	164.20	3.736	4.008	342.23	3450	2600		
TeEGMEb	208.25	4.481	4.061	353.23	3450	2600	-	-
DEGDMEb	134.17	3.300	3.955	308.15	-	-	-	-
TriEGDMEb	178.23	4.021	4.039	318.12	-	-	-	-
TeEGDME <sup>b</sup>	222.28	4.696	4.107	322.68	-	-	-	-
PEGDME250b *	250	5.130	4.140	326.43	-	-	-	-
CO <sub>2</sub> c	44.01	1.571	3.184	160.20	-	-	4.40	1/3

<sup>a</sup>- (Crespo et al. 2017) ; <sup>b</sup>- (Navarro et al. 2017) ; <sup>c</sup>- (Pedrosa et al. 2005); \*- Extrapolated from correlations.

## Results and Discussion

### Thermodynamic behavior of pure poly ethers (physical solvents)

The first application of soft-SAFT to the modelling of thermodynamic properties of polyether molecules was reported by Pedrosa et al. (Pedrosa et al. 2005), focused on the VLE of polyethylene glycol oligomers (from mono up to tetraethylene glycol). This early work showed good results when compared to experimental data. However, when the model and parameters were used to describe other properties than VLE the performance of the model deteriorated. We have recently demonstrated (Crespo et al. 2017) that a refined model, with molecular parameters fitted to VLE data, one isotherm of high pressure liquid densities and isothermal compressibilities (instead of just VLE data) provides more accurate results than the previous model. The results obtained showed that the new model was able to accurately describe simultaneously the VLE, the  $ppT$  and the rest of second order derivative properties not included in the fitting procedure. These results lead later to a further extension of the model to the description of glymes following a similar approach. (Navarro et al. 2017)

The vapor pressures and liquid densities of several polyethers are depicted in Figure 2 and as it can be seen, soft-SAFT is able to accurately describe such properties. Figure 2 a) shows that the introduction of hydroxyl end-groups within the polyethers structure decreases the vapor pressure of the compound due to the increased hydrogen bonding character of the compound that is retained in the liquid phase. For this reason,

the vapor pressures increase in the trend  $\text{DEGDME} > \text{DEGME} > \text{DEG}$  despite the increase in the compounds molecular weight. This behavior is well-captured by soft-SAFT and confirmed by the increasing values of association and dispersive energy that characterize these compounds, highlighting the greater physical meaning of the parameters and the consistent methodology applied to obtain them. In Figure 2 b) it can be observed that the liquid density of these polyethers generally decreases from glycols to mono-alkyl glymes, and from these to di-alkyl glymes or with the decrease of the polyethers molecular weight.

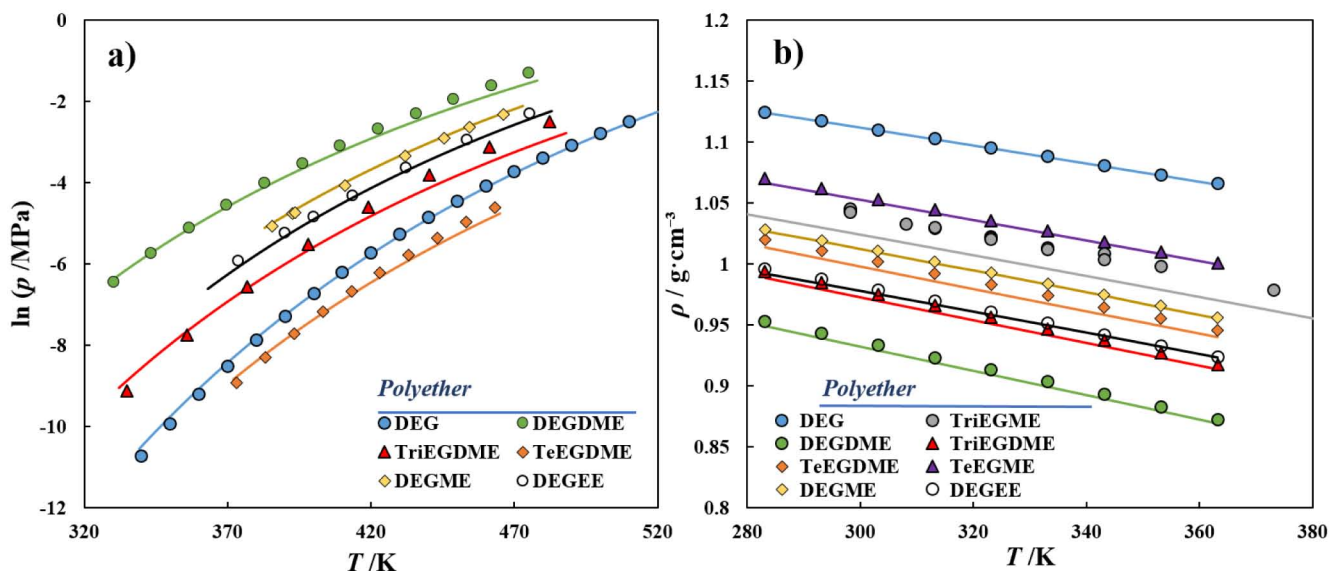


Figure 2— a) Vapor pressures and b) liquid densities at atmospheric pressure for several polyethers. The symbols represent experimental data (Henni et al. 1999, 2000; Crespo et al. 2017; Navarro et al. 2017) while the solid lines depict the soft-SAFT results.

As mentioned, the well-known transferability character of soft-SAFT, allows one to develop correlations between the non-associative pure-component parameters ( $m$ ,  $\sigma$  and  $\varepsilon$ ) and the molecular weight of the compound within the same homologous series. Therefore, the correlations previously proposed for mono-alkyl glymes (Navarro et al. 2017) were here applied, for the first time, to the prediction of the liquid densities of TriEGME (Fig. 2 b) – grey lines). As can be seen, soft-SAFT slightly underestimates the liquid densities of TriEGME when compared to the experimental data (Henni et al. 1999, 2000) but they are still predicted with a %ARD of 1.70 and the density values obtained are between those observed for TeEGME and those of DEGME as expected. The deviations to the experimental vapor pressures and liquid densities are reported in Table 2 and, as it can be seen, a remarkable fitting to the liquid densities was obtained for all the compounds with %ARD ranging between 0.05 and 0.38%. Higher deviations were observed for the vapor pressures with the %ARD considerably increasing (between 4.89 and 14.20%) with the polyethers chain length for which very low vapor pressures are observed and higher experimental uncertainties are acknowledged.

The good performance of soft-SAFT for the simultaneous description of temperature and pressure effects upon the thermodynamic behavior of polyethers is shown in Figure 3, where  $ppT$  data at three different temperatures is depicted for several polyethers. As it can be seen, the model is able to successfully describe the high-pressure densities in a wide temperature and pressure ranges without any systematic loss of accuracy. This allows the model to provide reliable predictions of other thermodynamic properties such as second-order derivative properties (which are highly sensitive to model inaccuracies, see, for instance, (Crespo et al. 2017) and references therein).

Table 2—Percentage average absolute relative deviations of the soft-SAFT modelling of the polyethers thermophysical properties.

Compound	%ARD ( $\rho$ )	%ARD( $\rho$ )	%ARD( $\rho pT$ )
DEG	6.44	0.05	0.06
DEGME	4.89	0.08	0.13
DEGEE	9.64	0.13	0.16
TriEGME	-	1.70	-
TeEGME	-	0.15	0.17
DEGDME	8.06	0.24	0.28
TriEGDME	14.20	0.29	0.34
TeEGDME	11.39	0.38	0.41

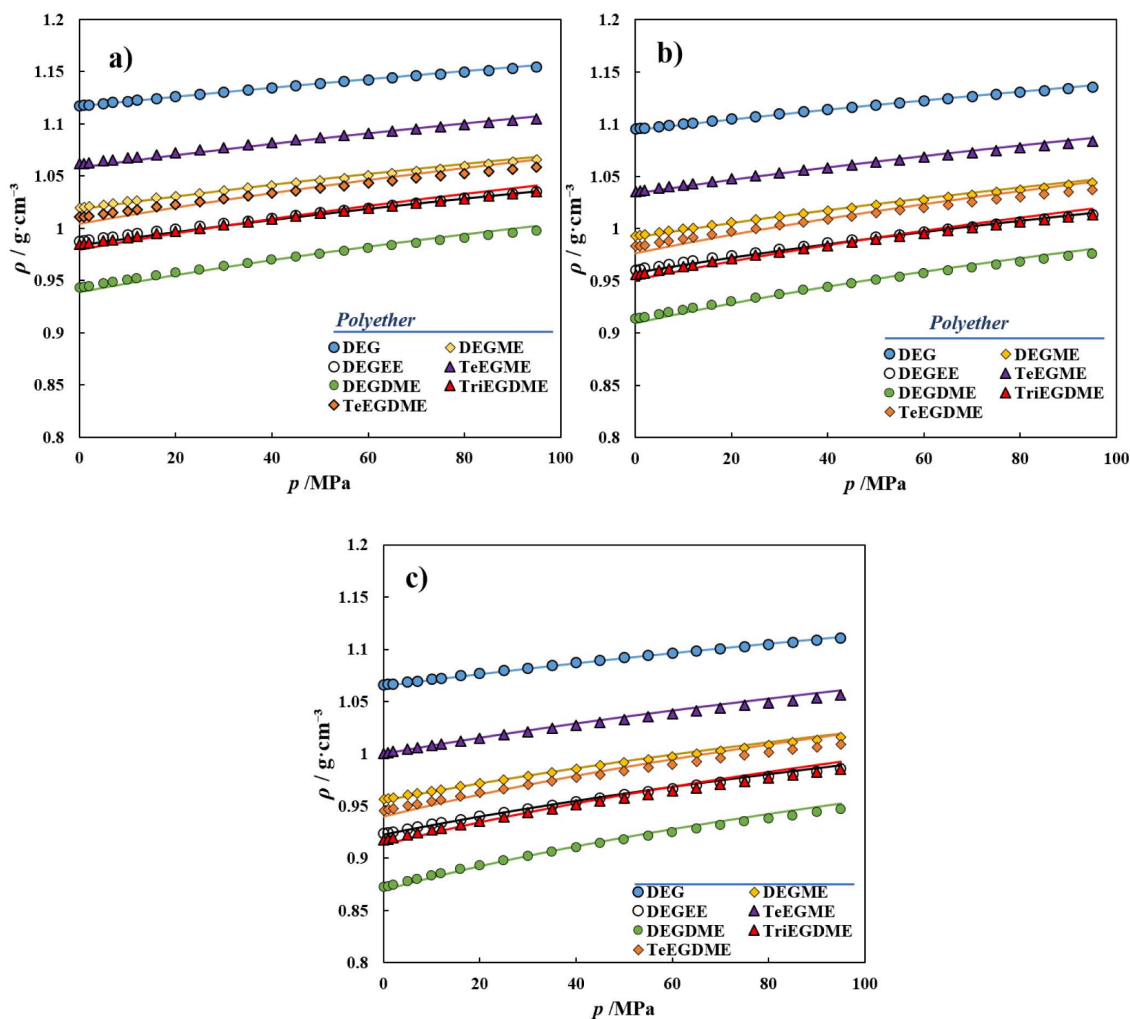


Figure 3—High pressure densities of several polyethers at a) 293.15K b) 323.15 K c) 363.15K. The symbols represent the experimental data (Crespo et al. 2017; Navarro et al. 2017) while the solid lines depict the soft-SAFT results.

### Gas/liquid equilibria of CO<sub>2</sub> + polyethers binary mixtures

Once the molecular models and parameters for both polyethers and carbon dioxide are established, soft-SAFT was used to study the phase equilibria behavior of their binary mixtures. Despite the known potential of polyethers as solvents for CO<sub>2</sub> capture, the experimental data available is, in most cases, still limited to very small temperature and pressure ranges. Solubilities of CO<sub>2</sub> in DEG are available in the temperature range 298.15-398.15 K (Jou et al. 2000). The performance of soft-SAFT in describing the GLE data is

shown in Figure 4 (left). By using one temperature dependent energy binary parameter,  $\xi$ , (see Equation 3), soft-SAFT is able to accurately describe the experimental data with a %ARD of only 5.61%. Moreover, the dependence of the binary parameter with temperature is weak with the values ranging between 0.975 at 298.15 K and 0.933 at 398.15 K, while seeming to approach an asymptotic value at high temperatures. As depicted in Figure 4 (right), such binary parameter is well correlated with temperature by a second-order polynomial given by Equation 7.

$$\begin{aligned}\xi_{DEG-CO_2} &= 3.314 \times 10^{-6} (T / K)^2 - 2.736 \times 10^{-3} T / K + 1.497 \\ R^2 &= 0.998\end{aligned}\quad (7)$$

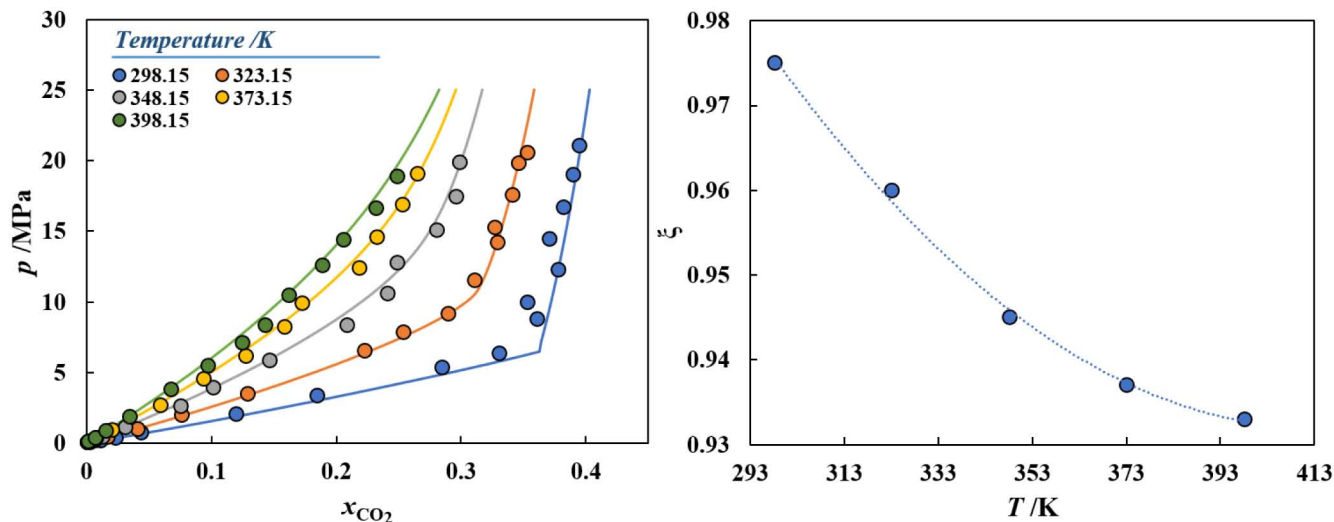


Figure 4—(Left) - Solubilities of CO<sub>2</sub> in DEG. The symbols represent experimental data (Jou et al. 2000) while the solid lines depict the soft-SAFT results using a temperature dependent binary parameter (right).

Kodama and co-workers (Kodama et al. 2011) measured the solubility of carbon dioxide in di-alkyl glymes (DEGDME, TriEGDME and TeEGDME) at 313.15 K and observed that as depicted in Figure 5, the solubility rapidly increases with pressure but it is rather insensitive to changes in the molecular weight of the glyme (and consequently on the number of ether groups). Nevertheless, it seems to have a cross-over point with the solubilities increasing as the chain length of the glyme is increased for the lower pressures, but with the opposite behavior at higher pressures. As depicted in the same figure, softSAFT is able to correctly predict this effect without the use of any binary interaction parameter ( $k_{ij}=0$ ), capturing the change in the shape of the solubility curve as the glymes chain length increases. Moreover, by applying very small corrections to the mixtures dispersive energy (binary interaction parameters in the range 1-1.04) a more accurate description of the experimental data can be obtained with a %ARD of 5.30, 4.42 and 2.80 for DEGDME, TriEGDME and TeEGDME respectively. In the same work, experimental values for the saturated densities were also reported and are depicted in Figure 6 for DEGDME+CO<sub>2</sub> along with the soft-SAFT results that are shown to be in good agreement with the softSAFT predictions.



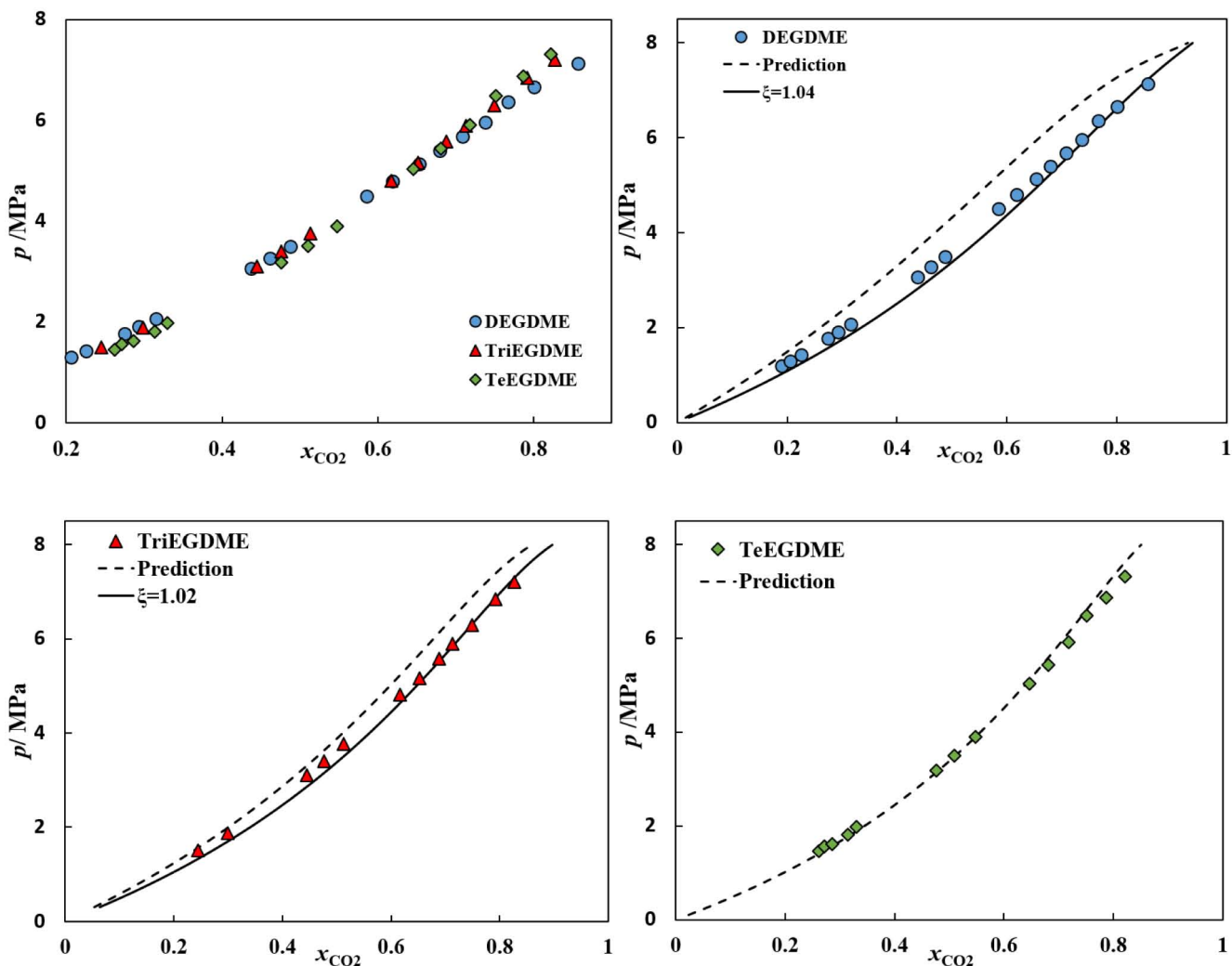


Figure 5—CO<sub>2</sub> solubilities in di-alkyl glymes at 313.15 K. The symbols represent experimental data(Kodama et al. 2011) while the dashed and solid lines depict the soft-SAFT predictions and fitting to experimental data respectively.

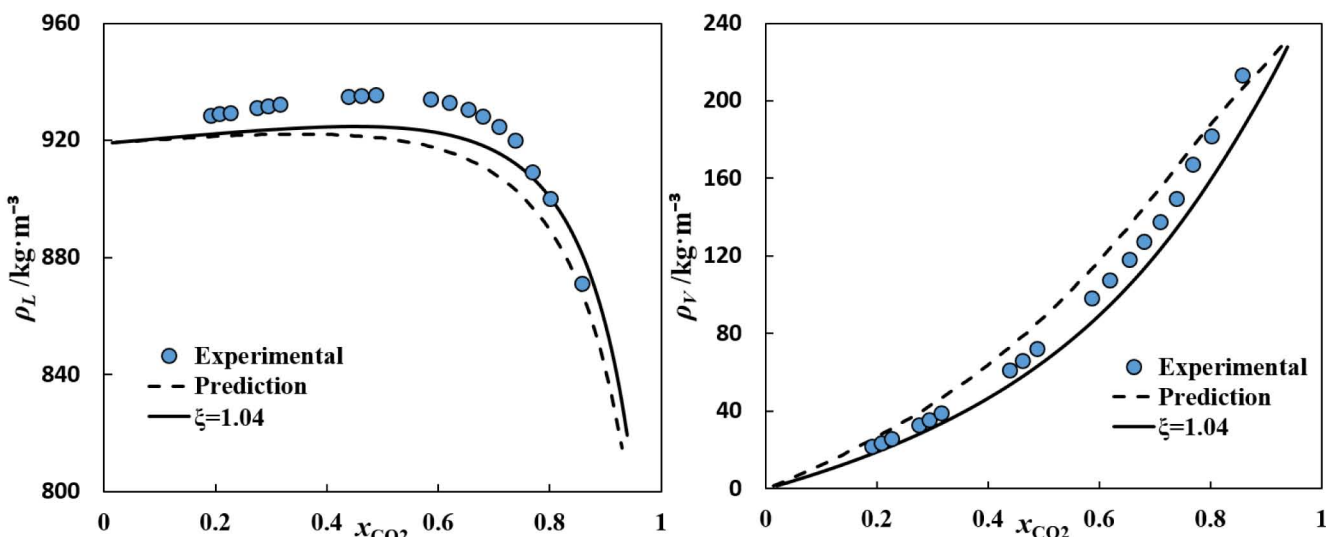


Figure 6—Saturated liquid (left) and vapor (right) densities of CO<sub>2</sub> in DEGDM. The symbols represent experimental data (Kodama et al. 2011) while the dashed and solid lines depict the soft-SAFT predictions and fitting to the CO<sub>2</sub> solubility data respectively.

Taking into account the transferability of soft-SAFT molecular parameters already discussed, the binary mixtures of CO<sub>2</sub> with a wider range of polyethers was next described. For instance, the correlations previously proposed for mono-alkyl glymes and di-alkyl glymes were used to obtain the molecular parameters for TriEGME and PEGDME250 (see Table 1) for which experimental gas-liquid equilibrium data with CO<sub>2</sub> is available. As depicted in Figure 7, soft-SAFT is able to accurately describe these systems using the predicted polyether parameters and using binary interaction parameters of the same magnitude to those applied for the remaining systems (1.025 for TriEGME and 0.98 for PEGDME250). Moreover, in these cases the binary parameter can be set independent of temperature allowing for an accurate description of these systems over a wide temperature range (up to 373 K) with a %ARD of 8.78 and 10.50 for TriEGME and PEGDME250, respectively. The need for a temperature dependent binary parameter in DEG, contrarily to what is observed in glymes, is probably related to the high influence of temperature upon the hydrogen bonding contribution that, as discussed, is more significant in glycols than in glycol ethers.

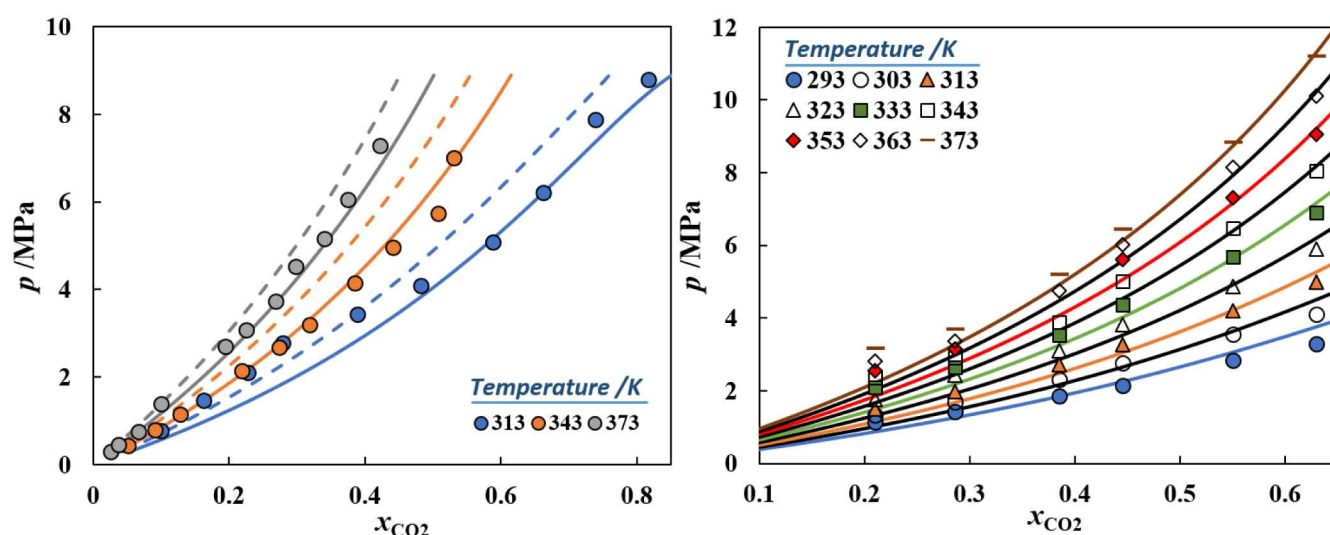


Figure 7—CO<sub>2</sub> solubilities as function of temperature for TriEGME (left) and PEGDME250 (right). Symbols represent experimental data (Henni and Mather 1995; Revelli et al. 2010), while the dashed and solid lines depict the soft-SAFT predictions and fitting to experimental data respectively.

The binary parameter applied to describe the phase equilibria of CO<sub>2</sub> + glymes binary mixtures was found to be correlated with the molecular weight of the glymes according to Equation (8). In spite of the fact that mono-alkyl glymes and di-alkyl glymes are modelled as two different families (with the latter being considered as non-associative), the binary parameter considered for the system with TriEGME fits well into the same correlation as those applied in the mixtures with di-alkyl glymes. As a reminder, this parameter is related to the asymmetry in the van der Waals interactions, not on the association, hence, the results obtained reinforce the consistency and reliability of the molecular model.

$$\xi_{glyme-CO_2} = -5.021 \times 10^{-4} M_{w\_glyme} / g \cdot mol^{-1} + 1.108 \quad (8)$$

$$R^2 = 0.990$$

As the aim of the work is to see the capability of soft-SAFT as a first step for assessing these solvents for CO<sub>2</sub> capture, we have also applied soft-SAFT to predict the thermal and pressure cycle capacities (TCC and PCC respectively) of the different solvents. TCC is here defined as the difference between the CO<sub>2</sub> solubilities in each polyether at two different temperatures at a given pressure, in order to evaluate their absorption/desorption capacity per cycle and to provide a comparison between them. Similarly, PCC is defined as the difference between the gas solubilities at two different pressures at a given temperature.

Therefore, the CO<sub>2</sub> solubilities at two different temperatures (298 and 373 K) were predicted using the binary parameters given by Equations (7)–(8) at a system pressure of 5 MPa and the results are presented in Table 3. As can be gauged from Table 3, the TCC of a polyether as a solvent for CO<sub>2</sub> seems to decrease with the introduction of hydroxyl end-groups in the solvents structure and with the increase of the molecular weight. Furthermore, the TCCs from the di-alkyl glymes (that generally show the higher TCC values) can be correlated with the molecular weight of the compound through Equation 9.

$$TCC_{d-alkyl\_glyme-CO_2} = -7.553^{-4} M_{w\_glyme} / g \cdot mol^{-1} + 0.5149 \quad (9)$$

$$R^2 = 0.9949$$

**Table 3—Thermal cycle capacities of different polyethers as predicted by soft-SAFT at 5MPa.**

Compound	$xCO_2@ 298K$	$xCO_2@ 373K$	TCC
DEG	0.2920	0.0996	0.1924
TriEGME	0.6974	0.3387	0.3587
DEGDME	0.8037	0.3910	0.4127
TriEGDME	0.7773	0.3970	0.3803
TeEGDME	0.7540	0.4033	0.3507
PEGDME250	0.7129	0.3897	0.3232

Analogously, the solubilities at two different pressures (0.1 and 7MPa) were predicted at 313.15 K and are reported in Table 4 along with the PCC values of each polyether which as observed for the TCCs, decrease with the introduction of hydroxyl end-groups in the chemical structure and with the polyethers chain length. The PCC values for the di-alkyl glymes can again be correlated with the glymes molecular weight according to Equation 10. The higher values of PCC when compared to TCC (~ 2x higher) show that the pressure effect is much stronger allowing for an easier absorption/desorption of CO<sub>2</sub>.

$$PCC_{d-alkyl\_glyme-CO_2} = -7.816^{-4} M_{w\_glyme} / g \cdot mol^{-1} + 0.9206 \quad (10)$$

$$R^2 = 0.9813$$

**Table 4—Pressure cycle capacities of different polyethers as predicted by soft-SAFT at 313 K.**

Compound	$xCO_2@ 0.1 MPa$	$xCO_2@ 7MPa$	PCC
DEG	0.0050	0.2825	0.2775
TriEGME	0.0186	0.7139	0.6953
DEGDME	0.0206	0.8349	0.8143
TriEGDME	0.0218	0.8026	0.7808
TeEGDME	0.0226	0.7771	0.7544
PEGDME250	0.0214	0.7411	0.7197

## Conclusions

Aiming at evaluating the performance of soft-SAFT as a thermodynamic tool for the design and simulation of new CO<sub>2</sub> capture processes, the modelling of the thermodynamic properties and phase behavior of pure polyethers and their binary mixtures with CO<sub>2</sub> was addressed by studying a set of different polyethers that allow for the evaluation of the impact of different structural effects, such as the chain length and the hydrogen bonding character of the solvent on the solubility behavior.

Using a molecular model that considers the polyethers as homonuclear chains with one association site per hydroxyl end-group, soft-SAFT was able to accurately describe the vapor pressures in a wide temperature range for the different compounds, capturing the decrease in the vapor pressure as the hydrogen bonding character of the polyether increases. The same model was also able to correctly describe the pressure and temperature effect upon the liquid densities of the different polyethers with %ARD ranging from only 0.06 to 0.41 % in the 293.15-363.15 K and 0.1-95 MPa temperature and pressure ranges. The transferability of soft-SAFT pure-component parameters was also addressed through the prediction of TriEGME liquid densities for which no experimental data was fitted. The values obtained were found to be between those of DEGME and TeEGME as expected.

The CO<sub>2</sub> solubilities in different polyethers were modeled explicitly considering the quadrupolar interactions. By using only one temperature and pressure independent binary parameter, that correlates with the molecular weight of the glyme, an accurate description of the phase behavior of CO<sub>2</sub> + glymes binary mixtures was obtained with %ARD ranging between 2.80% to 10.50%. Moreover, the model was also able to provide accurate estimates of the saturated densities (liquid and vapor), fundamental properties to the design and simulation of any novel process.

For DEG + CO<sub>2</sub> binary mixtures, due to the higher hydrogen bonding character of glycols when compared to glymes, a binary parameter very close to unity (weakly dependent on temperature) was necessarily applied in order to allow for an excellent description of the experimental data in a wide temperature (298-398 K) and pressure (0.1-22MPa).

Finally, soft-SAFT was applied to predict the thermal and pressure cycle capacities of the different solvents; these properties were found to decrease with the increase of the hydrogen bonding character of the solvent or with the increase in its chain length.

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