



Full Length Article

High-pressure solubility of CO₂ in glymes

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ABSTRACT

The study of carbon dioxide (CO₂) solubility in different solvents is important for the development of carbon capture and storage (CCS) technologies as well as for enhanced oil recovery (EOR) through CO₂ injection. Using two different experimental methodologies, based on the synthetic method, the high-pressure solubilities of CO₂ in four glymes, namely diethylene glycol methyl ether (DEGME), diethylene glycol dimethyl ether (DEGDME), diethylene glycol ethyl ether (DEGEE) and diethylene glycol diethyl ether (DEGDDEE) were measured in a wide range of temperatures (293–353 K) and pressures up to 13 MPa. Furthermore, the experimental CO₂ solubilities in the studied glymes were well described using the soft-SAFT EoS with parameters transferred from previous works, reinforcing its value as a reliable tool for the efficient simulation and design of new CCS/EOR technologies.

1. Introduction

Given the reckonable long-term prevalence of fossil fuels, as the main energy source, and the decline in the production of conventional oil, as a result of the physical depletion of the reservoirs, the Oil & Gas industry has been actively focused in the exploration, discovery and development of non-conventional resources and new technologies for enhanced oil and gas recovery. The discovery of pre-salt fields, with CO₂-rich oil and gas reservoirs (typically 8–12% [1]) but that can reach 75% in specific blocks, stands out as the largest oilfield discovery in the last decade, initiating a new era of oil exploration with striking challenges and requiring ground-breaking developments. Environmental impact driven by the naturally produced CO₂ ventilation rose special concerns, making the major oil companies involved in the exploration of these fields announce their commitment not to vent the CO₂ produced, although conscious that CO₂ separation units are expensive and challenging to operate.

The Oil & Gas industry is thus, compelled to pursue novel Carbon Capture and Storage (CCS) technologies, able to mitigate their share in the world's greenhouse gases emissions, and develop low cost plants with reduced footprints, weight and energy consumption aiming at a sustainable hydrocarbon production. Special attention has been given to the *in loco* CO₂ capture, usage as enhanced oil recovery agent and, ultimately, sequestration in the reservoir. Although current CO₂

separation units are expensive and impose important space and weight requirements, the development of new sustainable units, would fulfill the sector's expectation while allowing to overcome the unavailability of economic supplies of CO₂ for the enhanced oil recovery [2–4].

Built on top of Selexol (mixture of dimethyl ethers of polyethylene glycols) process success, the low cost, low viscosity, high boiling point, easy availability, and high CO₂ solubilities of glymes have attracted special interest as physical solvents for gas sweetening. However, in spite of being important for the design of the Selexol process, the CO₂ high-pressure phase equilibrium of glymes + CO₂ binary mixtures is surprisingly scarce [5,6].

The limited experimental data on high-pressure solubilities of CO₂ in glymes, hinders the development of accurate thermodynamic models able to describe the phase equilibria and thermophysical properties required for the design, optimization and development of industrial processes. Cubic equations of state (EoS) are the standard models in the oil industry however, they exhibit a limited accuracy for complex systems involving associating (e.g. polyethers) or polar (e.g. CO₂) molecules. Conversely, molecular-based EoS derived from statistical mechanics (e.g. SAFT-type equations [7–9]), explicitly account for such molecular interactions providing a better physical interpretation of the system arising as the future standard for engineering purposes. Among the different SAFT variants [10,11], soft-SAFT is one of the most successful due to its ability to consistently describe the phase equilibrium

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and thermophysical properties for a wide range of compounds from a limited amount of experimental data. Moreover, soft-SAFT has been successfully applied to describe gas solubilities in different associating solvents including water [12], ionic liquids [13–15], amines [16] and polyethers [17,18], in very good agreement with experimental data.

In this work the high-pressure solubilities of CO₂ in four different glymes are measured using two different experimental methodologies based on a visual synthetic method in a wide range of temperatures, pressures and compositions. The experimental data measured was then described using the soft-SAFT EoS providing some insights into the key molecular properties leading the solubility behavior.

2. Experimental

2.1. Materials

Diethylene glycol methyl ether (DEGME), diethylene glycol dimethyl ether (DEGDME), diethylene glycol ethyl ether (DEGEE), and diethylene glycol diethyl ether (DEGDEE) were obtained from Sigma-Aldrich Co. with mass fraction purities higher than 99%. The compounds were further purified to remove traces of water, by using 3 Å zeolites. The final water content was determined with a Metrohm 831 Karl Fisher coulometer, which was found to be lower than 100 ppm. Carbon dioxide was acquired from White Martins (≥99.9%) and Air Liquide (≥99.998%) for the pressure decay and pressure rise methodologies, respectively.

2.2. Solubility measurements

Two different methodologies and apparatus were used to determine the CO₂ solubility in the selected glymes. Both apparatuses are based on the synthetic method and consist of a horizontal hollow stainless-steel cylinder, closed at one end by a movable piston and at the other end by a sapphire window, from which the operator follows the behavior of the system, with known composition, with pressure [19]. The first method, hereinafter referred as *Constant Pressure Decay* (CPD) method, consists on starting from a homogeneous phase and reducing the system pressure, at a constant decay rate of 0.2 MPa.min⁻¹, until the appearance of the first bubble is observed. The apparatus and methodology adopted are fully described in previous publications [20–22] and consist of a syringe pump (Teledyne ISCO, 260D), filled with propane, to control the system pressure and a type J thermocouple, with an uncertainty of 0.1 K placed inside the cell, in contact with the sample, to monitor the temperature. The high-pressure cell is able to operate for pressures up to 30 MPa and in the (273–373 K) temperature range. The system's pressure is monitored by measuring the pressure of the compressor fluid (propane) by means of a pressure transducer (NOVUS, TP HUBA) with an uncertainty of 0.01 MPa. The sample's compositions are prepared by adding to a fixed and known amount of glyme (measured by a Shimadzu AX 200 balance with an uncertainty of 0.0001 g) known amounts of CO₂, using a second syringe pump connected to a cell inlet. During the initial preparation, the glyme is placed in the high-pressure cell and the air inside removed by the gas phase suction.

The second method, hereinafter referred as *Constant Equilibrium Pressure* (CEP) method, also promotes a phase change from a homogeneous to a biphasic system that, although not controlled in terms of pressure decay, is managed to promote only a small amount of released gas. The pressure is then increased and maintained constant to determine if the selected pressure is enough to dissolve all the CO₂. The methodology is repeated, trying in each new attempt a lower equilibrium pressure, until the tested pressure is no longer able to completely dissolve the gas. The system's equilibrium pressure, for that specific composition, is thus, the pressure measured in the previous cycle and the lowest able to dissolve all the gas. This CEP cell is fully described in previous publications [14,23,24] and is able to operate up to 100 MPa

and in the (293–363 K) temperature range. The cell is thermostated by circulating a heat-carrier fluid, thermo-regulated using a thermostat bath circulator (Jubalo MC F25) with a temperature stability of 0.01 K, through three flow lines directly managed into the cell. The temperature inside the cell is measured by a type K thermocouple, with an uncertainty of 0.15 K, placed close to the sample and the pressure is measured by a piezoresistive silicon pressure transducer (Kulite HEM 375) fixed directly inside the cell to reduce dead volumes with accuracy better than 0.2%.

In both apparatuses, an external magnetic stirrer and a magnetic bar placed inside the cell are used to assure a complete homogenization of the mixture.

3. Soft-SAFT modelling

3.1. The soft-SAFT Equation

Soft-SAFT[25], as most SAFT-type equations [9,26], is given as an expression for the residual Helmholtz energy (A^{res}) as the summation of different molecular contributions:

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

In Eq. (1), A^{ref} is the contribution due to both the repulsive and attractive interactions between the monomers (segments) forming a chain, given by a Lennard-Jones (LJ) EoS described by Johnson et al. [27] from molecular simulation data. A^{chain} , is a contribution due to the formation of chains from individual monomers and is based in the thermodynamic perturbative approach of Wertheim [28–31]. A^{assoc} accounts for strong, short range and highly directional forces such as hydrogen-bonding (also derived from Wertheim's theory) while, A^{polar} is an additional term that can be considered when dealing with strong polar molecules like CO₂, to deem polar and multipolar interactions. A more detailed description of each one of these terms and detailed expressions can be found in the soft-SAFT's original papers [10,11].

To fully characterize a non-associating chain-like molecule i , three molecular parameters are required, namely the segment's diameter (σ_i) and the dispersive energy between segments (ϵ_{ii}/k_B) from the reference term and the number of monomers or chain length (m_i) from the chain formation term. As the reference term is for the pure LJ fluid, the extension to mixtures is accomplished applying the van der Waals one-fluid theory with the unlike size and energy LJ parameters given by means of the Lorentz-Berthelot mixing rules:

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

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

In Eqs. (2) and (3), η_{ij} and ξ_{ij} are the size and energy binary interaction parameters between species i and j , being equivalent to the $(1-l_{ij})$ and $(1-k_{ij})$ binary parameters used in most cubic EoSs. These parameters (fitted to mixture data) account for the differences in size and/or energy of the monomers composing the different compounds in the mixture. Consequently, when using the EoS in a full predictive manner, both η_{ij} and ξ_{ij} are set to one, and mixture calculations are done with pure component parameters.

When dealing with associating compounds two additional parameters are required, related to the energy (ϵ_{ii}^{HB}/k_B) and bonding volume (κ_{ii}^{HB}) of the association sites. The general extension to mixtures requires the evaluation of cross-association energies and volumes given by the following expressions:

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

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

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

| Compound | Mw (g/mol) | m_i | σ_i (Å) | ε_{ij}/k_B (K) | ε^{HB}/k_B (K) | κ^{HB} (Å ³) | $10^{40} Q_{exp}$ (C·m ²) | x_p | Ref |
|-----------------|--------------|-------|----------------|----------------------------|----------------------------|---------------------------------|---------------------------------------|-------|------|
| DEGME | 120.15 | 2.995 | 3.889 | 330.50 | 3450 | 2600 | – | – | [32] |
| DEGEE | 134.17 | 3.165 | 4.009 | 331.00 | 3450 | 2600 | – | – | [32] |
| DEGDME | 134.17 | 3.300 | 3.955 | 308.15 | – | – | – | – | [32] |
| DEGDDE | 178.23 | 3.586 | 4.165 | 309.43 | – | – | – | – | [32] |
| CO ₂ | 44.01 | 1.571 | 3.184 | 160.20 | – | – | 4.40 | 1/3 | [17] |

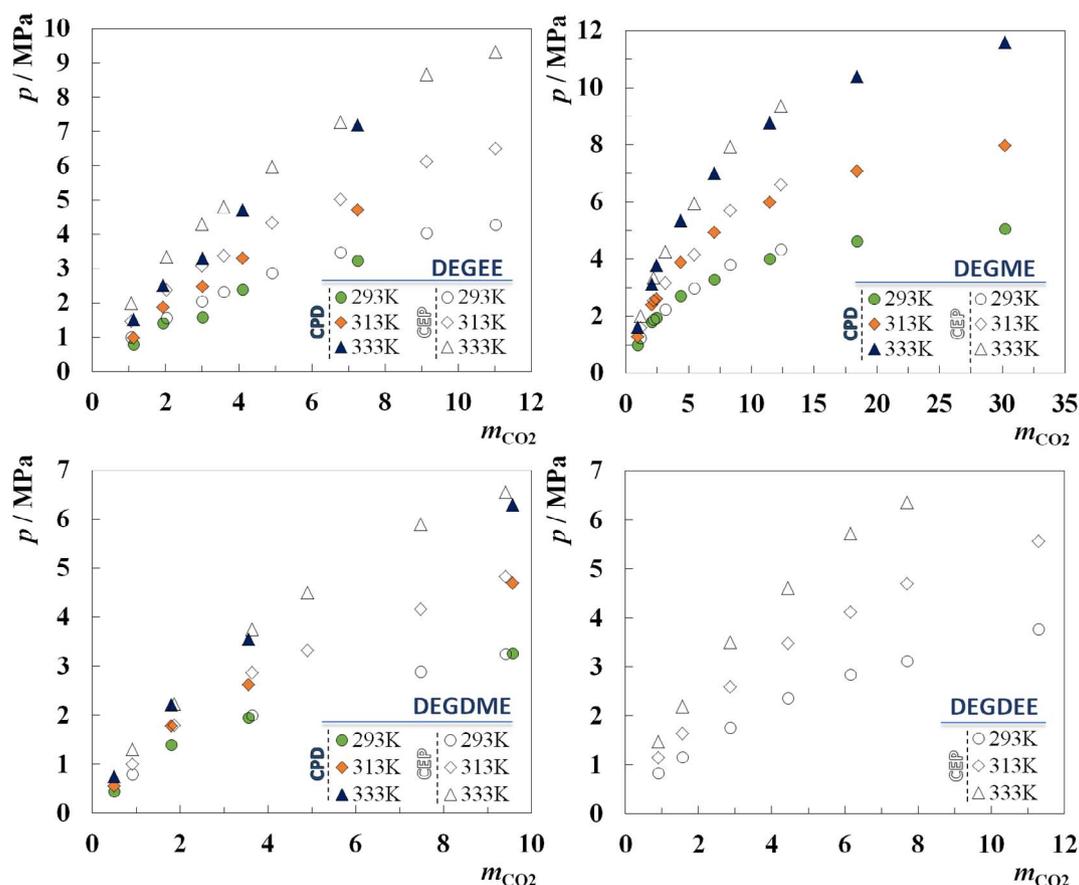


Fig. 1. pTm_{CO_2} phase diagram for the binary systems CO₂ + DEGEE, DEGME, DEGDME and DEGDDE. The full and empty symbols represent the CPD and CEP methods, respectively.

For polar molecules, the polar term includes an effective quadrupole moment (Q), that is related to the experimental multipolar moment through a parameter x_p [17], fixed a priori as the fraction of segments in the chain that effectively contains the polar moment:

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

3.2. Molecular models

The performance of molecular-based EoSs like soft-SAFT rely on the adequate selection of a molecular model (and association scheme) capable of representing most of the compounds physical features. Therefore, besides the pure-component parameters required to describe each compound, the number, type of association sites and allowed interactions, within the system, need to be specified a priori depending on the system under investigation.

Recently, Navarro et al. [32] proposed a molecular model for glymes, considering one single association site per each hydroxyl end-group, while implicitly accounting for the effects due to the lone pair of electrons in each oxygen of the ethylene oxide groups through the effective values of the parameters. Despite its simplicity, the model accurately described several pure-component properties and was easily

transferable to compounds not included in the fitting procedure. Therefore, the same model is adopted here in a transferable manner, assessing its applicability to mixtures of glymes with CO₂. Following our previous work CO₂ was modelled as a non-associating LJ chain in which the polar interactions are explicitly taken into account [17].

Hence, the soft-SAFT pure-component parameters used in this work in a transferable manner are summarized in Table 1 for completeness.

4. Results and discussions

The CO₂ solubility in the selected glymes was measured for mole fractions ranging from 0.05 to 0.75, in the temperature range 293.15–353.15 K and pressures up to 13 MPa, as reported in Table S1 through S4, available in the Supporting Information. As depicted in Fig. 1, the two experimental adopted methodologies are in good agreement, presenting deviations similar to those commonly observed in the literature. For the DEGEE, however, increasing deviations were observed, with higher CO₂ solubilities being obtained through the CPD method.

Notwithstanding glymes relevance to a large number of industries and applications, especially for CCS, their gas-liquid equilibrium with CO₂ is poorly studied. Among the data available in literature, Henni

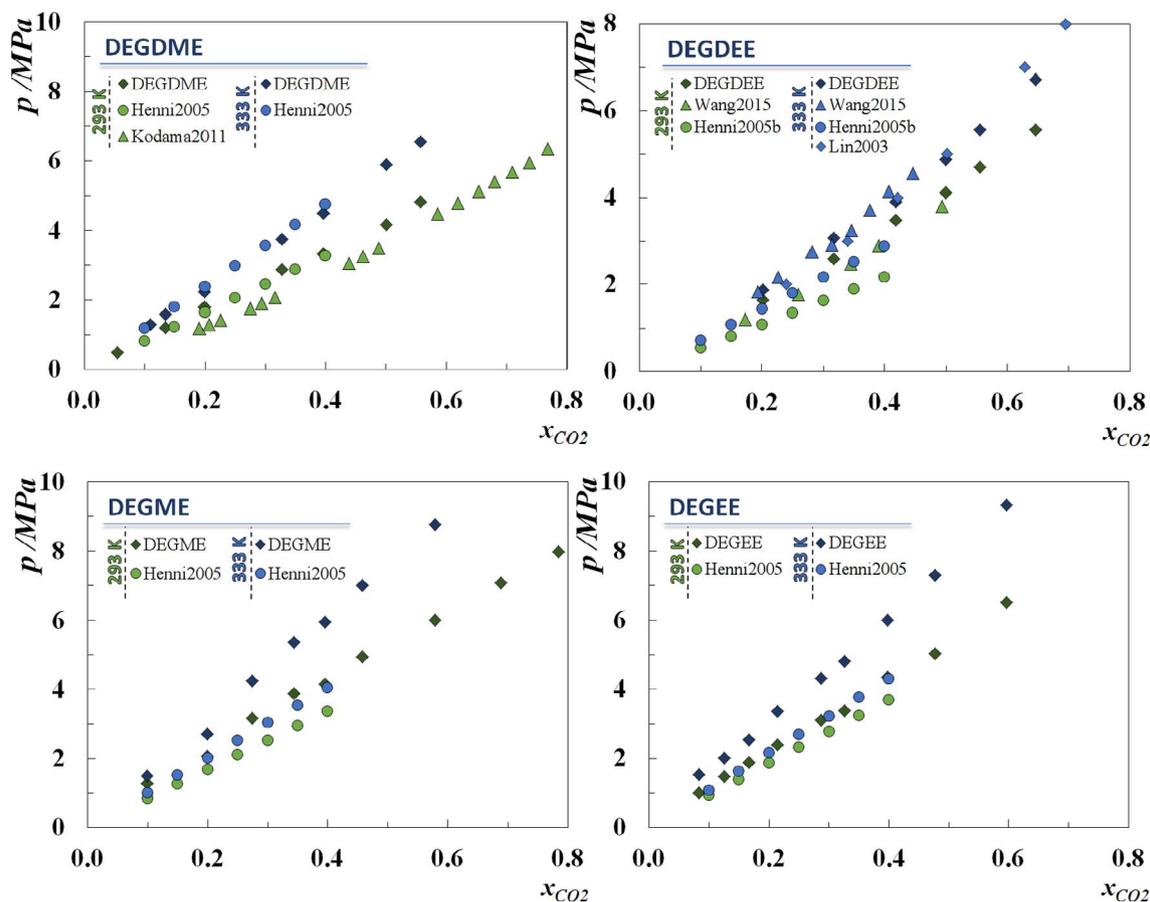


Fig. 2. Pressure-composition diagram of the binary systems CO₂ + DEGDME, DEGDEE, DEGEE and DEGME as measured in this work (diamonds) and literature comparison.

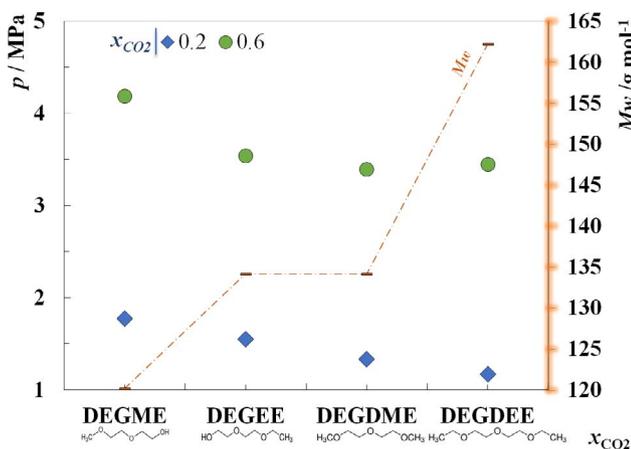


Fig. 3. Pressure-composition diagram of the binary systems CO₂ + glymes at 293 K and CO₂ mole fractions of 0.2 and 0.6.

Table 2
Binary interaction parameters used in the soft-SAFT calculations and deviations with respect to the experimental data.

| CO ₂ + | η_{ij} | ξ_{ij} | %AAD |
|-------------------|-------------|------------|------|
| DEGME | 1.028 | 0.995 | 3.86 |
| DEGEE | 1.028 | 0.974 | 6.62 |
| DEGDME | 1.028 | 0.991 | 3.70 |
| DEGDEE | 1.028 | 0.960 | 5.93 |

et al. [33] reported Henry’s constants at 298, 313 and 333 K for DEGME, DEGEE and DEGDME. For DEGDME, Sciamanna et al. [34] and Kodama et al. [35] reported Henry’s constants and equilibrium pressures at 313 K and 298 K for pressures ranging from 1 to 7 MPa, respectively. For DEGEE, Wang et al. [36] reported equilibrium pressure for CO₂ mole fractions up to 0.5 and for DEGDEE Lin et al. [37] reported VLE data at 333, 373 and 413 K for gas mole fractions up to 0.8. As depicted in Fig. 2, a good agreement is observed for all the systems whose experimental data is available at similar gas compositions and equilibrium pressures. The pressure and composition ranges investigated here do not allow determining the compound Henry’s constant with adequate uncertainty for a direct comparison with those reported in the literature and, therefore, an extrapolation of the equilibrium pressures for gas compositions within those investigated here would lead to large deviations as those depicted in Fig. 2, the only exception is DEGDME whose data extrapolated from Henni et al. [33] Henry’s constants present a similar linearity to that observed for the experimental data.

As depicted in Fig. 3, the solubility of CO₂ in the studied glymes increases with the molecular weight. Furthermore, the substitution of one hydrogen in the hydroxyl group by an ethyl or a methyl group leads to a decrease on the equilibrium pressures, as observed for the DEGME and DEGDME and DEGEE and DEGDEE. The decrease of the glyme’s hydrogen-bonding ability has several consequences in the systems behavior: lowering of the magnitude of the interactions between the glymes, increasing the system free volume, enhancing the interactions with the CO₂ and thus, leading to an increase on the gas solubilities, as observed for the case of DEGEE and DEGDME isomers. Nonetheless, the temperature increase weakens the observed behaviors, leading to smaller increases on the solubility.

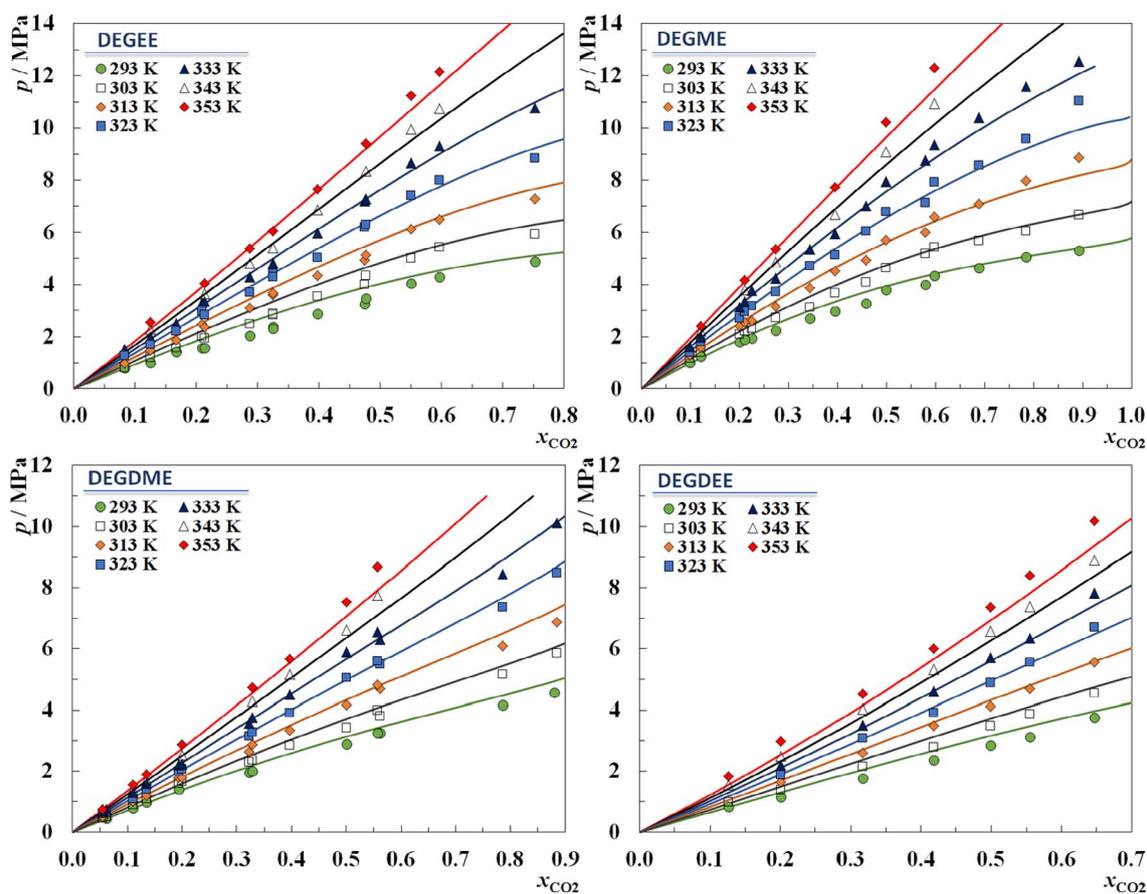


Fig. 4. Pressure-composition diagram of the binary systems CO₂ + DEGEE, DEGME, DEGDME and DEGDEE. The solid lines represent the soft-SAFT results using temperature independent binary interaction parameters (see Table 2).

Soft-SAFT's ability to successfully describe the phase equilibria of complex systems containing polar and/or associative compounds as those studied in this work, was here evaluated on the description of the experimental data. As reported in Table 2, two binary interaction parameters (η_{ij} correcting the unlike segment size diameter and ξ_{ij} correcting the magnitude of cross-dispersive interactions), very close to unity, were used to achieve a good qualitative description of the data as depicted in Fig. 4. Although size binary parameters are generally avoided when dealing with mixtures with similar chemical groups, huge size differences between the compounds length and their sparse sphericity may require the use of a size binary parameter to achieve a good description of the data, while allowing for a decrease in the correction triggered by the energy binary parameter. Nevertheless, one of the main advantages of using molecular-based EoSs is that their parameters are usually independent of state conditions such as temperature and pressure. In this work, the high-pressure phase diagrams calculated with soft-SAFT were obtained with a state-independent η_{ij} ($=1.028$) parameter across the four systems studied. The value of the parameter, greater than one, indicates that the volume occupied by the molecules in the mixture is higher than the ideal case (Lorentz-Berthelot's rule with $\eta_{ij} = 1$). The energy binary parameter was fitted to the experimental data at 323 K for each mixture and transferred for the remaining temperatures. Values lower than unity were observed in all cases suggesting a higher unlike interaction in the mixture than the one predicted by the ideal case (Lorentz-Berthelot's rule with $\xi_{ij} = 1$). Moreover, the ξ_{ij} values were found to decrease with the increase of the glyme's chain length and/or with the removal of the hydroxyl end-group, the latter being expected because of the simplifications within the glyme's molecular model that by considering DEGDME and DEGDEE as non-associative species resulted in increased values of dispersive energy.

5. Conclusions

The CO₂ solubility in DEGEE, DEGME, DEGDME and DEGDEE was measured for mole fractions ranging from 0.05 to 0.75, in the temperature range 293.15–353.15 K and pressures up to 13 MPa using two different experimental methodologies, based on the synthetic method. The methodologies adopted have shown good agreement with deviations similar to those commonly observed in the literature between different methodologies and to the literature data, at similar gas compositions and equilibrium pressures.

As commonly observed, the solubility of CO₂ increases with the glyme molecular weight but, the substitution of one hydrogen in the hydroxyl group by an ethyl or a methyl group, decreasing thus the glyme's hydrogen-bonding ability, leads to a decrease on the equilibrium pressures and increased CO₂ solubility.

Soft-SAFT was used to describe the phase equilibria of measured data, with molecular parameters and models transferred from previous works. The model successfully describes the behavior of the mixtures under study, with a binary size parameter constant for all mixtures, and an energy binary parameter for each mixture, both of them temperature independent. The use of soft-SAFT with these parameters sheds some lights on the type of interactions between the glymes and CO₂, helping in the engineering design of CO₂ capture systems.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.fuel.2018.01.084>.

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