

Exploring alternative solvents for gas processing using the soft-SAFT EoS

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Summary

Polyethers are a family of compounds of interest for the oil industry: glycols are known by their application as dehydration agents while glymes have gained the interest from both industry and academia as feasible candidates for gas separations. However, their characterization is still poor, hindering the development and optimization of novel separation processes. This work aims at demonstrating the soft-SAFT reliability that, when combined with a limited number of experiments, can provide a way for systematic studies on the performance of physical solvents for gas processing technologies. A recently developed, consistent, reliable and transferable molecular model for polyethers in the framework of soft-SAFT, is here applied for the first time to model the vapor-liquid equilibria (VLE) of glymes + CH₄/CO₂. Moreover, the same model is shown to be able to accurately describe the VLE of aqueous solutions of polyethers.

Introduction

Given the world's population growth and consequent increase on the global energy demand, the Oil & Gas industry plays a vital role in today's society, not only because oil and gas are important energy sources but also because they serve as feedstocks for a wide number of industries. On the other hand, the environmental impact driven by their activities establishes an endless demand for cleaner and more efficient technologies that can result in the development of low-cost plants of reduced emissions, weight and energy consumption. The development and optimization of such technologies is a demanding but inspiring task, closely tight to the development of novel solvents for gas separations and, consequently, to an accurate understanding of the sorption and permeation mechanism of the reservoir gases.

Raw natural gas is much different than end-use natural gas, which is composed almost entirely by methane (CH₄). Regardless of the natural gas source, methane is generally present in a hydrocarbons mixture (mainly C₂ to C₅) along with water vapor, carbon dioxide (CO₂), hydrogen sulfide (H₂S), nitrogen (N₂) and other gases. Therefore, and prior to distribution, the gas needs to be processed, aiming at the removal of the different gases and hydrocarbons from CH₄ to meet the required pipeline specifications.

Among the different solvents used in these separations, polyethers are a family of special interest. For instance, low molecular-weight glycols like diethylene glycol (DEG) and triethylene glycol (TriEG) are used as dehydration agents to remove water from a natural gas stream while, blends of polyethylene glycol dimethyl ethers (glymes) are used to the selective removal of H₂S and CO₂.(Carvalho et al. 2015) The design of industrial plants using these solvents requires an accurate thermodynamic tool that allows a consistent and robust description of different thermodynamic properties and phase equilibria (e.g. VLE) for systems containing polyethers.

Activity coefficient models and/or cubic equations of state (EoSs) with simple mixing rules are generally employed by the oil industry, however they usually fail when applied to describe the thermodynamic behavior of complex fluids such as those containing polar (CO₂) and/or associating molecules (e.g. glycols, glymes). Alternatively, the Statistical Associating Fluid Theory (SAFT) and its variants, such as soft-SAFT, with a strong physical background, are able to explicitly account for effects such as the molecular shape and molecular interactions (including short-range and highly directional hydrogen-bonding as well as electrostatic interactions). Due to the robustness, consistent and predictive character of SAFT models, they are progressively replacing cubic EoS for designing purposes as they allow for systematic studies on the influence of the molecular structure on the phase equilibria behavior.(Tan et al. 2008) This work aims at demonstrating the value of soft-SAFT EoS as a generic thermodynamic model for gas processing applications by evaluating the performance of this equation when used to describe the thermodynamic properties of pure polyethers and their vapor-liquid equilibria with CH₄, CO₂ or H₂O.

soft-SAFT Equation of State (EoS)

SAFT (acronym for Statistical Associating Fluid Theory) is a successful thermodynamic approach based on statistical thermodynamics concepts such as the first-order thermodynamic perturbation theory (TPT1), (Wertheim 1984a, b) that was later proposed in the form of an engineering EoS by Chapman et al. (1989, 1990). In the framework of SAFT, molecules are viewed as a number of spherical segments interacting by covalent bonds forming chains that might associate at specific bonding sites (see schematic representation in **Fig. 1**). The residual Helmholtz free energy of a fluid system (A^{res}) – **eq 1** – is thus obtained

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as a sum of different contributions; each corresponding to a different structural or energetic effect: a reference term (A^{ref}) that accounts for the segment-segment interactions; a chain term (A^{chain}) to account for the formation of chains from the individual segments and an association term (A^{assoc}) that considers hydrogen bonding. When dealing with strong polar molecules like CO_2 , an additional term (A^{polar}) can be added. Once the residual Helmholtz energy of a system is obtained, one can easily derive all the thermodynamic properties and fugacity coefficients (necessary for phase equilibria calculations) by using only derivatives and ideal gas integrals.

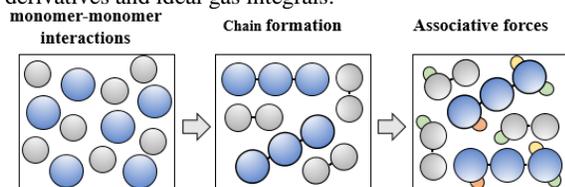


Figure 1. Schematic representation of the physical foundation of SAFT-type equations.

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

Although SAFT-type equations use the same chain and association term proposed by Wertheim, modifications to the original model, differing on the reference term have been proposed. Among them, soft-SAFT, (Blas and Vega 1997) that considers a Lennard-Jones (LJ) intermolecular potential for the reference fluid, stands out due to its ability to successfully describe the thermodynamic behavior of distinct families of compounds (e.g. water, polyethers, amines, ionic liquids, refrigerants...) and its performance when used to describe the gas solubilities in different physical solvents.

To fully characterize an associating compound i , five physically meaningful pure-component parameters, usually regressed from experimental vapor pressures and density data, are required by the model:

- m – number of segments constituting the chain.
- σ – the segment's diameter.
- ϵ_{ii} / k_B – dispersive energy between segments.
- ϵ_{aa}^{HB} and κ_{aa}^{HB} – association energy and volume between two α associating sites.

The extension to mixtures is carried under the van der Waals one-fluid theory with the unlike parameters calculated using the generalized Lorentz-Berthelot mixing rules:

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

$$\epsilon_{ij} = \xi_{ij} \left(\frac{\epsilon_{ii} + \epsilon_{jj}}{2} \right) \quad (3)$$

Completing the molecular model, an association scheme needs to be defined a priori to all associating molecules, specifying the number and type of association sites, as well as the interactions allowed in the system in order to mimic the associating forces that may be present in the real fluid. When describing molecules with a strong polar moment such as CO_2 and N_2 , the inclusion of the polar term introduces two additional parameters, namely the experimental quadrupole moment (Q_{exp}) and the fraction of segments that effectively contain the quadrupole (x_p).

Both CH_4 and CO_2 were modelled using soft-SAFT in previous works with the parameters being used here in a transferable manner. CH_4 was modelled as a non-associating single spherical segment (Pàmies and Vega 2001) while CO_2 was modeled as a LJ chain in which the quadrupolar interactions were explicitly taken into account. (Pedrosa et al. 2005)

Recently, we developed a simple yet effective molecular model for polyethers by considering them as LJ chains composed of spherical segments of equal size with one associating site (type A) per each hydroxyl group present in the molecule's structure while allowing for AA interactions. (Crespo et al. 2017; Navarro et al. 2017) As the model was built upon the knowledge successively acquired by studying simpler and similar chemical families, the influence of each change in the chemical structure of a given molecule in the values of the molecular parameters could be better understood, allowing, in the end, to mimic the hydrogen bonding behavior of the ethylene oxide groups present in the polyether molecules (glycols or glymes) through the specific values of the parameters, avoiding the use of additional associating sites and the consequent increase on the computational cost of subsequent calculations.

The resulting molecular model was found to provide a very good description of pure polyethers properties (e.g. vapor pressures, saturated densities, high-pressure liquid densities and second-order derivative properties such as the isothermal compressibility and isobaric thermal expansion). (Crespo et al. 2017; Navarro et al. 2017) Moreover, and due to the physical meaning of the parameters, the model was found to be transferable to compounds not used in the fitting procedure, as the non-associating molecular parameters can be obtained by correlations built from the first members of each family as a function of the molecular weight, as depicted in **Figure 2** for glycols. The association volume and energy are generally kept constant for the whole series as the hydrogen bonding interactions are not greatly influenced by the chain length after the first or two first members of the chemical family. This allows the model to be fully predictive as the pure-component parameters to any polyether (e.g. those for which no experimental data is available) can be obtained from the correlations developed for glycols and glymes. (Crespo et al. 2017; Navarro et al. 2017)

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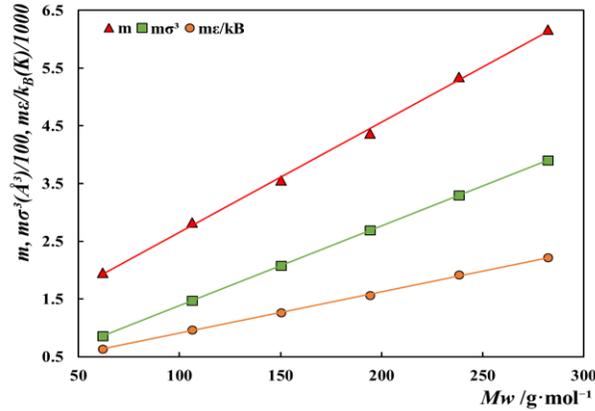


Figure 2. soft-SAFT molecular parameters as a function of the glycol's molecular weight.

Results

The methane solubility in selected glymes was measured experimentally in the temperature range (293-353 K) and pressures up to 20 MPa. **Fig. 3** illustrates the experimental solubility measured in triethylene glycol dimethyl ether (TriEGDME) and diethylene glycol ethyl ether (DEGEE) along with the soft-SAFT modelling using the molecular parameters transferred from previous works as reported in **Table 1**. As depicted, and in accordance to what was previously observed in other solvents such as ionic liquids, (Carvalho and Coutinho 2011) the temperature effect in the CH_4 solubility is negligible, with soft-SAFT being able to capture such behavior using one state-independent binary interaction parameter, whose value, although increasing with the solvent's molecular weight, is only marginally influenced by the glyme considered (e.g. $\xi=0.915$ for TriEGDME and 0.90 for DEGEE). The value of the energy parameters applied, which are lower than unity, highlight the existence of weak interactions between CH_4 and glymes, reinforcing the positive deviations to ideality that characterize these mixtures (note that for ideal mixtures, $\xi=1.0$). Moreover, soft-SAFT was able to predict, in the correct range of pressures, the inversion point of the methane solubility due to its supercritical state.

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

	m_i	σ_i (Å)	ε_{ii}/k_B (K)	ε^{HB}/k_B (K)	κ^{HB} (Å ³)	$Q_{exp} \cdot 10^{40} x_p$ (C·m ²)
TriEGDME ^a	4.021	4.039	318.12	-	-	-
DEGEE ^a	3.165	4.009	331.00	3450	2600	-
CH_4 ^b	1.000	3.728	147.20	-	-	-
CO_2 ^c	1.571	3.184	160.20	-	-	4.40 1/3

^a-(Navarro et al. 2017) ^b-(Pàmies and Vega 2001) ^c-(Pedrosa et al. 2005)

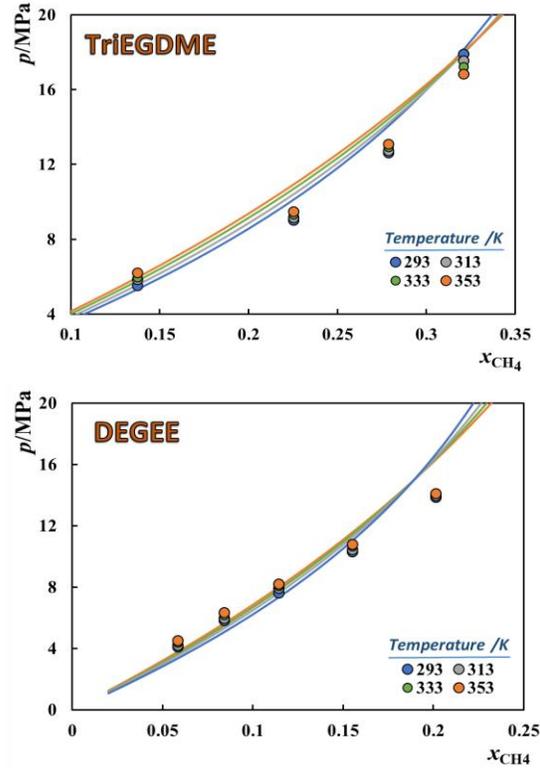


Figure 3. CH_4 solubilities in TriEGDME and DEGEE in the 293-353 K temperature range. The symbols represent experimental data while the solid lines depict the soft-SAFT results.

The oxygenation of alkyl chains is a known approach to enhance the CO_2 sorption. A number of studies in the literature highlight the favorable interactions of oxygen with CO_2 . (Carvalho et al. 2016) As depicted in **Fig. 4**, a much higher solubility of carbon dioxide in glymes is observed, allowing glymes to be used for a selective separation of gases. soft-SAFT is able to accurately describe the experimental data and the much stronger temperature effect upon the gas solubility using two temperature independent binary interaction parameters (η_{ij} and ζ_{ij}) very close to unity. The size-related binary parameter, η_{ij} is further transferable across different glymes. Given the good performance of soft-SAFT to describe the solubilities of gases in glymes, it can be used to obtain the ideal gas selectivities ($S_{\text{CO}_2/\text{CH}_4}$) through **eq.4** using the Henry's constants calculated from the soft-SAFT EoS as the limiting slope of the solubility curve as the gas composition approaches zero.

$$S_{\text{CO}_2/\text{CH}_4} = \frac{H_{\text{CH}_4\text{-glyme}}}{H_{\text{CO}_2\text{-glyme}}} \quad (4)$$

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This is illustrated in Fig. 5 for DEGDEE and as it can be observed, glymes are very selective towards CO₂ with the selectivity decreasing with increasing temperature since, although the CH₄ solubility is temperature independent, the CO₂ solubility greatly decreases as the temperature increases.

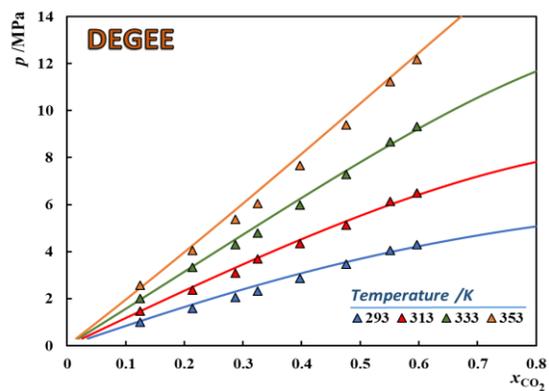


Figure 4. CO₂ solubilities in DEGEE as a function of temperature. Symbols represent the experimental data while the solid lines depict the soft-SAFT results using $\eta_{ij}=1.028$ and $\zeta_{ij}=0.974$.

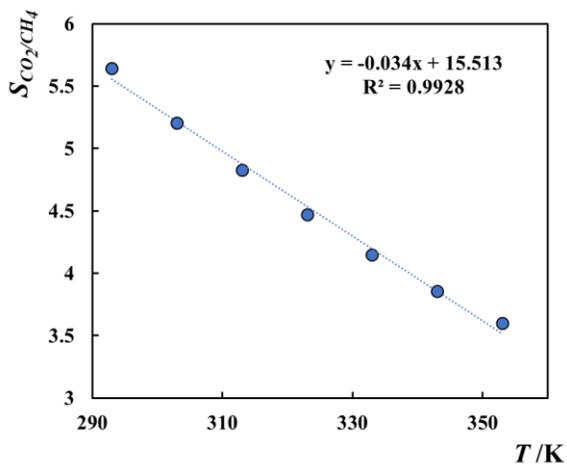


Figure 5. Ideal gas selectivity CO₂/CH₄ for DEGEE.

The same molecular model can be applied to describe the VLE of aqueous solutions. The experimental boiling temperatures of binary mixtures DEGEE + H₂O and triethylene glycol (TriEG) + H₂O is depicted in Fig. 6 along with the soft-SAFT results. Using a temperature and pressure independent binary parameter ($\zeta_{ij}=1.145$ and $\xi_{ij}=1.175$), an excellent agreement with the experimental data is observed. Similar, accurate results are obtained regardless the glycol or glyme under consideration, even for high molecular weight glycols not used in the model parameterization.

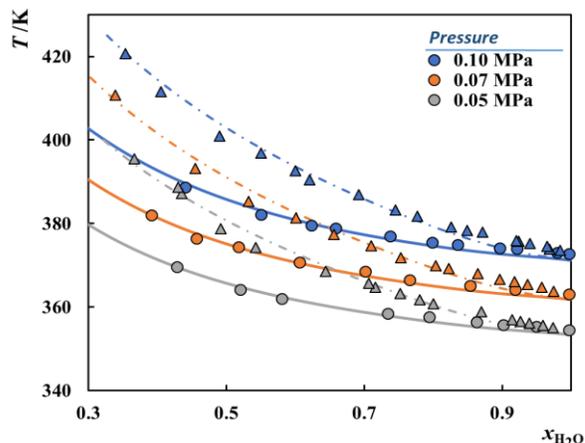


Figure 6. Boiling point temperatures of DEGEE + H₂O (●) and TriEG + H₂O (▲). Symbols depict the experimental data while the solid and dotted-dashed lines represent the soft-SAFT results for the mixture with DEGEE and TriEG respectively.

Conclusions

This work builds upon previous works aiming at evaluating the performance of soft-SAFT EoS as a thermodynamic model useful for Oil & Gas applications. A molecular model for polyethers previously developed and showed to be accurate to describe different thermodynamic properties of polyethers is here applied for the first time to the modelling of gas solubilities (CH₄/CO₂) in glymes and used to obtain their respective enhanced selectivity as a function of temperature. Furthermore, the model can also be applied to model the VLE of aqueous solutions of polyethers with an excellent agreement with the experimental data being obtained in all cases.

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References

- Blas, F. J., and L. F. Vega, 1997, Thermodynamic behaviour of homonuclear and heteronuclear Lennard-Jones chains with association sites from simulation and theory: *Molecular Physics*, **92**, 135–150, doi: 10.1080/002689797170707
- Carvalho, P. J., and J. A. P. Coutinho, 2011, The polarity effect upon the methane solubility in ionic liquids: a contribution for the design of ionic liquids for enhanced CO₂/CH₄ and H₂S/CH₄ selectivities: *Energy & Environmental Science*, **4**, 4614–4619, doi: 10.1039/C1EE01599K
- Carvalho, P. J., C. H. G. Fonseca, M-L. C. J. Moita et al. , 2015, Thermophysical Properties of Glycols and Glymes: *Journal of Chemical & Engineering Data*, **60**, 3721–3737, doi: 10.1021/acs.jced.5b00662
- Carvalho, P. J, K. A. Kurnia, and J. A. P. Coutinho, 2016, Dispelling some myths about the CO₂ solubility in ionic liquids: *Physical Chemistry Chemical Physics* , **18**, 14757–14771, doi: 10.1039/C6CP01896C
- Chapman, W. G., K. E. Gubbins, G. Jackson, and M. Radosz, 1989, SAFT: Equation-of-state solution model for associating fluids: *Fluid Phase Equilibria* , **52**, 31–38, doi: 10.1016/0378-3812(89)80308-5
- Chapman, W. G., K. E. Gubbins, G. Jackson, and M. Radosz, 1990, New reference equation of state for associating liquids: *Industrial & Engineering Chemistry Research*, **29**, 1709–1721, doi: 10.1021/ie00104a021
- Crespo, E. A., J. M. L. Costa, Z. B. M. A. Hanafiah, et al., 2017, New measurements and modeling of high pressure thermodynamic properties of glycols: *Fluid Phase Equilibria*, **436**, 113–123, doi: 10.1016/j.fluid.2017.01.003
- Navarro, P., E. A. Crespo, J. M. L. Costa, et al., 2017, New Experimental Data and Modeling of Glymes: Toward the Development of a Predictive Model for Polyethers: *Industrial & Engineering Chemistry Research*, **56**, 7830–7844, doi: 10.1021/acs.iecr.7b01532
- Pàmies J. C., and L. F. Vega, 2001, Vapor–Liquid Equilibria and Critical Behavior of Heavy n - Alkanes Using Transferable Parameters from the Soft-SAFT Equation of State: *Industrial & Engineering Chemistry Research*, **40**, 2532–2543, doi: 10.1021/ie000944x
- Pedrosa N., J. C. Pàmies, J. A. P. Coutinho, et al., 2005 Phase equilibria of ethylene glycol oligomers and their mixtures: *Industrial & Engineering Chemistry Research*, **44**, 7027–7037, doi: 10.1021/ie050361t
- Tan S. P., H. Adidharma, and M. Radosz, 2008, Recent Advances and Applications of Statistical Associating Fluid Theory: *Industrial & Engineering Chemistry Research*, **47**, 8063–8082, doi: 10.1021/ie8008764
- Wertheim, M. S., 1984a, Fluids with highly directional attractive forces. I: Statistical thermodynamics. *Journal of Statistical Physics*, **35**,19–34, doi: 10.1007/BF01017362
- Wertheim, M. S., 1984b, Fluids with highly directional attractive forces. II: Thermodynamic perturbation theory and integral equations, *Journal of Statistical Physics*, **35**, 35–47, doi: 10.1007/BF01017363