

Phase Equilibria of Ethylene Glycol Oligomers and Their Mixtures

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We present and discuss the influence of the molecular architecture on the phase equilibria behavior of ethylene glycol oligomers and their mixtures based on predictions from a molecular-based equation of state (EoS). The soft statistical associating fluid theory (SAFT) EoS is used to fit the molecular parameters from the available vapor liquid experimental data, providing a correlation of the molecular parameters with the molecular weight of the compounds, which can be used to predict the behavior of heavy members of the series. The same equation is used to describe the ethylene glycol oligomer mixtures with several compounds, including carbon dioxide, benzene, methane, and *n*-hexane. The performance of the soft-SAFT equation is compared with some Gibbs excess free energy models and the Peng–Robinson EoS, where soft-SAFT is superior in most of the cases. Once the performance of the equation and the molecular model are established, soft-SAFT is used as a predictive tool to systematically study the influence of the chain length, polarity, and hydrogen bonding formation on the behavior of two selected mixtures. The influence of the oligomers' chain length is noticeable in the dew points of liquidlike solutes (benzene), with almost no effect in the boiling point of these mixtures, except for the ethylene glycol mixture. On the contrary, the solubility of carbon dioxide on these oligomers strongly depends on chain length, increasing as the alkyl part of the chain increases. This is attributed to the breaking of hydrogen bonds in the shorter oligomers.

1. Introduction

The use of ethylene glycol (EG) and its oligomers such as diethylene glycol (DEG), triethylene glycol (TEG), and tetraethylene glycol (TeEG) has been increasing in industry for the past few years. Their main use is in the petroleum industry as an inhibitor of the formation of gas hydrates due to their low vapor pressure and their high solubility in water. Another common use of ethylene glycols is as solvents for the selective removal of aromatic hydrocarbons from naphtha.¹ Thus, the knowledge of the vapor–liquid equilibria (VLE) behavior of the relevant mixtures of ethylene glycol oligomers in separation processes in which they are used is extremely important. In addition, it will help in the design of the optimal conditions of application of larger molecules, such as polyethylene glycol (PEG), from a fundamental point of view. Unfortunately, experimental data on these oligomer systems is rather scarce. In fact, to our knowledge, no systematic study on the influence of chain length and/or molecular architecture on the solubility of different compounds has been performed to date. In addition, the complexity of these mixtures presents a challenge to any modeling approach. Hence, it would be desirable to have a reliable theoretical tool in which the influence of these different variables can be checked.

Much effort has been devoted in recent years toward the development of molecular-based equations of state

(EoS), mainly due to their ability to predict the behavior of complex fluids and/or extreme conditions, for which other classical methods fail. Among these predictive methods, the statistical associating fluid theory (SAFT)^{2–4} is becoming very popular in academic and industrial environments due to its success in predicting the behavior of a wide variety of industrial relevant mixtures. This theory has generated a series of different versions of what are now known as SAFT-type equations, based on Wertheim's first-order thermodynamic perturbation theory (TPT1).^{5–8} The most popular version of this equation is that developed by Huang and Radosz.⁴ These authors parametrized the equation for several pure fluids and mixtures showing its applicability for real engineering applications from its development. Although the equation has some known limitations and some of the provided fitted parameters lack of physical meaning, it is straightforward to implement and relatively easy to use. Other recent, more refined, modifications of SAFT include the soft-SAFT equation of Vega and co-workers,^{9–11} the SAFT-VR equation of Jackson and co-workers,¹² and the PC-SAFT equation of Sadowski and co-workers.¹³ All SAFT-type equations use Wertheim's theory for the chain and association term, while they differ mainly in the reference term. A detailed discussion on the success and limitations of SAFT equations, improvements, and applications can be found in two excellent reviews published on the subject.^{14–15}

The objective of this work is to perform a systematic study of the influence of the molecular architecture on the solubility of several compounds in EG oligomers from a modeling approach. For this purpose, we use the soft-SAFT equation;^{9–11} the predictive power and ac-

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curacy of soft-SAFT has been recently checked with experimental systems for which cubic-type EoSs fail, such as the solubility of hydrogen in heavy *n*-alkanes¹⁶ and the solubility of gases in perfluoroalkanes.^{17,18} We first propose a molecular model for each of the compounds; molecular parameters are obtained by fitting to the available VLE data. Special care is taken on the meaning of the parameters and the possible transferability of them. A correlation of the molecular parameters with the molecular weight of the compounds is proposed for EG oligomers, which can be transferred to long molecules, including PEG. The performance of soft-SAFT in describing VLE for mixtures is assessed by comparing its results with experimental data for several systems. Phase equilibria for some of these systems are also estimated using other molecular models, namely, Gibbs excess free energy (G^E)-based models (sUNIQUAC¹⁹) and the Flory Huggins (FH) theory, which have proved to be accurate for complex mixtures. The Peng–Robinson (PR) EoS²⁰ is also used for comparison, chosen as a benchmark equation because of its use as standard in process simulation on chemical industry. Finally, we use soft-SAFT with the molecular parameters obtained here to study the solubility of two selected systems, benzene and carbon dioxide, on different EG oligomers, as a function of the their chain length. No comparisons with other refined versions of SAFT^{12,13} are performed since, in principle, no qualitative differences should be expected with respect to soft-SAFT as applied to these type of mixtures: the physical ingredients are similar in the three equations, and in all of them some parameters are fitted. What it would slightly change would be the particular values of these parameters, depending on the equation used (i.e., the energy parameter has not an exact mapping in a square-well fluid and in a Lennard-Jones (LJ) fluid when representing the same real substance).

2. Theory

2.1. Soft-SAFT Modeling. The general expression for SAFT is given in terms of the residual Helmholtz energy, A^{res} , defined as the molar Helmholtz energy of the fluid relative to that of an ideal gas at the same temperature and density. This residual Helmholtz energy can be obtained as the sum of the different microscopic contributions. For the systems investigated in this work, the general expression of the SAFT equation is

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

The reference term, A^{ref} , usually describes the properties of the individual units that compose the chain. Different versions of SAFT use different terms for the reference fluid, such as hard spheres with a perturbative term, to take into account the dispersive forces,² square-well spheres of variable range,¹² LJ spheres,^{10,21} or perturbed hard chains.¹³

In this work, we use a spherical LJ fluid as the reference fluid, and its contribution to the total free energy of the system is obtained from the accurate equation of state of Johnson et al.²² The equation is extended to mixtures using the van der Waals one-fluid theory (vdW-1f).²³ For the determination of unlike parameters, the generalized Lorentz–Berthelot com-

binning rules are employed

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

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

where η and ξ are the binary adjustable parameters for the species *i* and *j*. As shown in the previous expressions, it is possible to explicitly separate deviations in molecular size from deviations in energy, by fitting both. It is also possible to account for all deviations with a single binary parameter. The advantage would be that there is only one binary parameter to fit, and the disadvantage would be that this only parameter would account for both, resulting in greater deviations from unity, the ideal value.

The chain term, A^{chain} , accounts for the energy of formation of chains from units of the reference fluid. This term is obtained taking the limit of complete bonding in Wertheim's TPT1, and it is formally identical in all versions of SAFT. The Helmholtz free energy due to the formation of chains from m_i spherical segments can be written as

$$A^{\text{chain}} = RT \sum_i x_i (1 - m_i) \ln g_{LJ} \quad (4)$$

where $R = k_B N_A$ is the ideal gas constant, k_B the Boltzmann constant and N_A the Avogadro's number, x_i the molar fraction of component *i*, m_i its chain length, and g_{LJ} is the radial distribution function of a LJ mixture of spheres at contact length σ . We use the g_{LJ} function fitted to simulation data provided by Johnson et al.²⁰ Note that this contribution is readily applicable to mixtures.

The association term, A^{assoc} , is added when the fluid under study has an associating behavior (i.e., possible formation of hydrogen bonds). The association Helmholtz free energy depends mainly on X^α , the fraction of molecules not bonded at site α . The computation is performed over all association sites on the molecule and for all associating species present in the mixture

$$A^{\text{assoc}} = RT \sum_i x_i \left[\sum_\alpha \ln X^\alpha_i - \frac{X^\alpha_i}{2} + \frac{M_i}{2} \right] \quad (5)$$

$\alpha = A, B, C, \dots$

where M is the number of association sites per molecule, α is the running label for the association sites, which are labeled with capital roman letters, and the sum extends over all *i* compounds in the mixture. The specific expression for X^α can be found in ref 9. It relates the number of bonded molecules (or nonbonded molecules) to two molecular parameters, ϵ_{HB} and k_{HB} , the energy of the association site and the volume of association, respectively.

The number of association sites for each molecule, as well as the allowed interactions among the sites, has to be specified a priori within the SAFT approach. In this work, we consider all association interactions to be equivalent, i.e., all sites have the same values for the ϵ_{HB} and k_{HB} parameters.

The leading multipole term for fluids of linear symmetrical molecules, such as carbon dioxide, acetylene, etc., is the quadrupole–quadrupole potential,²⁴ which introduces a new parameter, the quadrupole moment

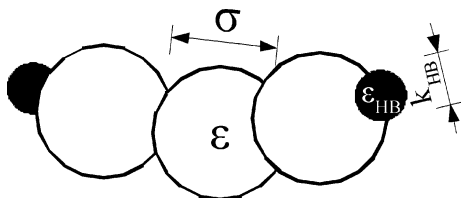


Figure 1. Schematic representation of a TEG-like molecule.

Q , for each compound able to show this type of electrostatic interactions. An expansion of the Helmholtz free energy in terms of the perturbed quadrupole–quadrupole potential with the Padé approximation was proposed by Stell et al.²⁵

$$A^{qq} = A_2^{qq} \left(\frac{1}{1 - \frac{A_3^{qq}}{A_2^{qq}}} \right) \quad (6)$$

Expressions for A_2 and A_3 , the second- and third-order perturbation terms, were derived for an arbitrary intermolecular reference potential and can be found in the original papers.^{24–27}

All relevant terms to the present work are listed above. Additional terms can be added to further improve the abilities of the equation, such as dipolar terms²⁸ or electrolyte terms (mean spherical approximation, MSA)²⁹ or even a density gradient theory (DGT) to study interfacial properties,^{30,31} making this model very modular and flexible.

To apply the soft-SAFT equation, a molecular model for each of the compounds integrating the mixture needs to be proposed. We model EG and its oligomers as LJ chains with one associating site at each end group. The molecular parameters to be obtained by fitting to experimental data are: m , the chain length; σ , the segment size; ϵ , the dispersive energy of interaction; and ϵ_{HB} and k_{HB} , the energy and volume of association per site, respectively. Figure 1 shows as an example a cartoon of the molecular model used for the triethylene glycol molecule.

The quadrupolar interactions present in systems with carbon dioxide, benzene, and nitrogen need to be taken into account in a molecular modeling approach. These electrostatic interactions have been modeled with and without the inclusion of the quadrupolar term in SAFT-type equations. In the second case, the quadrupolar contribution is *effectively* included in the value of the other molecular parameters;³² this would be a valid approach, since all parameters are effective; however, it does not allow the investigation of the explicit contribution the quadrupole has to the global behavior of the mixture. In the case of explicit inclusion of quadrupolar interactions, which is the approach taken in this work, a new parameter, Q , needs to be taken into account. The formalism used to model this kind of interaction is the one proposed by Twu and Gubbins.²⁴ The quadrupolar moment is modeled being effectively present in a fraction of the segments of the molecule (x_p), i.e., one-third of the carbon dioxide molecule actually “carries” the quadrupole moment. The value of the molecular parameter Q is obtained in the usual way, by fitting to experimental data. However, care is taken so that the chosen value of Q is sound as compared to that found by experimental or ab initio methods. The fraction x_p is chosen depending on the molecules’ geometry.

With x_p and Q fixed, only the usual three molecular parameters need to be adjusted for the quadrupolar molecules (CO₂, benzene, and nitrogen) as it happens for the nonquadrupolar molecules (hexane, propane, and methane): m , the chain length, and σ and ϵ , the size and energy parameters of the groups forming the chain. These three parameters are fitted in each case to experimental VLE data for the pure compounds or taken from previous work.

2.2. Gibbs Excess Free Energy Models. Since the experimental data of EG oligomer mixtures is scarce and reliable models are needed, in addition to soft-SAFT, we have decided to investigate the performance of other well-established models for these mixtures. In particular, we have used the FH model and a modified UNQUAC model¹⁹ as representative of G^E kind of models. The objective is to compare the performance of the soft-SAFT EoS against these conventional models. A brief summary of the main equations used here is presented below.

In the FH model, the molecules of the fluid mixture are assumed to be disposed on a lattice. The model derives its combinatorial term from the number of possible states for the distribution of the molecules on the lattice. The modified FH model where a residual contribution is added to the combinatorial term can be written for component 1 in a binary mixture as³³

$$\ln \gamma_1 = \ln \left(\frac{\phi_1}{x_1} \right) + 1 - \left(\frac{\phi_1}{x_1} \right) + \chi \phi_2^2 \quad (7)$$

The fitting parameter χ takes into account enthalpic and entropic contributions. It is obtained by adjusting to VLE data.

The sUNQUAC model is based on the local composition theory. It was specially developed to model binary mixtures of very asymmetric mixtures such as polymer solutions. The equation has the following form¹⁹

$$\ln \gamma_1 = \ln \left(\frac{\phi_1}{x_1} \right) + 1 - \left(\frac{\phi_1}{x_1} \right) - q_1 \ln(X_1 + X_2 \tau_{21}) + X_2 q_1 \left(\frac{\tau_{21}}{X_1 + X_2 \tau_{21}} - \frac{\tau_{12}}{X_2 + X_1 \tau_{12}} \right) \quad (8)$$

where τ is described by

$$\tau_{ij} = e^{a_{ij}/RT} \quad (9)$$

The a_{ij} term is the energy term that is adjusted to experimental VLE data.

2.3. The PR Equation. Since the PR²⁰ EoS is widely spread in the academic and industrial environments, we also use it here as a benchmark equation provided for reference. The equation can be written as

$$P = \frac{RT}{V-b} - \frac{a(1-m(1-\sqrt{T_r}))^2}{V(V+b) + b(V-b)} \quad (10)$$

where

$$a = 0.45723553 \frac{R^2 T_c^2}{P_c} \quad (11a)$$

$$b = 0.07779607 \frac{RT_c}{P_c} \quad (11b)$$

$$m = 0.37464 + 1.54226\omega - 0.26993\omega^2 \quad (11c)$$

where $T_r = T/T_c$ is the reduced temperature, T_c and P_c the critical temperature and pressure of the given fluid, respectively, R the universal gas constant, and ω the Pitzer factor, which essentially takes into account the nonsphericity of the molecules. The equation can be applied to mixtures with the usual vdW-1f theory, and mixing rules are applied as follows

$$a = \sum_i \sum_j x_i x_j \sqrt{a_i a_j} \zeta_{ij} \quad (12a)$$

$$b = \sum_i \sum_j x_i x_j \left[\frac{1}{2}(b_i + b_j) \right] \delta_{ij} \quad (12b)$$

where the ζ_{ij} and δ_{ij} are the binary interaction parameters that are fitted to mixture data. Usually ζ_{ij} is represented by $(1 - k_{ij})$ in most cases where the equation is used. We have used this particular notation for a straightforward comparison with soft-SAFT. Critical properties to use with the PR EoS were taken from the NIST webbook,³⁴ and the Pitzer factor was taken from the book published by Elliot and Lira.³⁵ In the case of the ethylene glycols, the determination of the Pitzer factor was taken from pure component data with the following expression

$$\omega = \log P_r^\sigma |_{T_r=0.7} - 1.0 \quad (13)$$

3. Results and Discussion

The performance of the soft-SAFT EoS, as well as sUNQUAC and FH methods for the description of EG, DEG, TEG, and TeEG and the mixtures of EG + CO₂, EG + N₂, EG + C₆H₆, DEG + CO₂, TEG + C₆H₆, TEG + C₆H₁₄, TeEG + CO₂, TeEG + C₆H₆, is addressed. Experimental data for these mixtures was taken from different sources available in the literature.^{1,36–40} Experimental VLE data was first used to fit the molecular parameters of the different pure compounds required by soft-SAFT, establishing a correlation for the molecular parameters of EG oligomers as a function of their molecular weight. These parameters were then used to check the accuracy of the soft-SAFT EoS for predicting the mixture behavior as well as for searching trends in the solubility behavior as a function of the molecular weight and/or thermodynamic conditions.

3.1. Pure Components. The molecular parameters m , σ , and ϵ for EG, DEG, TEG, and TeEG, obtained by fitting the available VLE data,⁴¹ are presented in Table 1. The association parameters (ϵ_{HB} and k_{HB}) were fitted to EG VLE data, and their values were fixed for the rest of the oligomers. The maximum AAD was obtained for TEG (4.18%), being that the other deviations are well inferior to that value. To get visual information on the

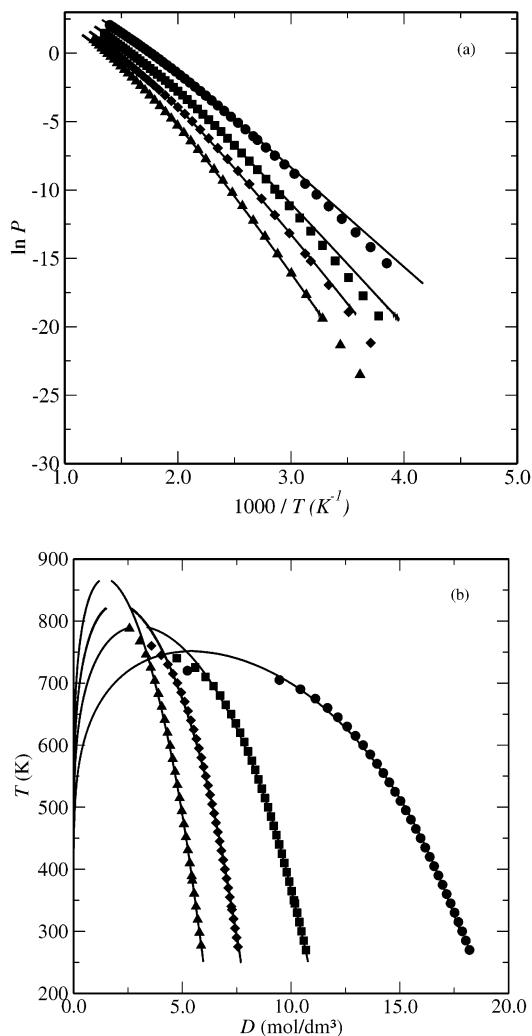


Figure 2. (a) Logarithm of the vapor pressure vs the reciprocal of temperature and (b) vapor and liquid density as function of temperature of the EG oligomers (EG (●), DEG (■), TEG (◆), and TeEG (▲)). Symbols represent the experimental data,³⁶ while the line corresponds to the soft-SAFT modeling.

accuracy of these fittings, the experimental vapor pressure and density–temperature data are plotted along with the description of the soft-SAFT model in parts a and b of Figure 2, respectively. As shown in the figures, the fitting is excellent, except near the critical point. This was expected, since we are using an analytical equation of state, in which the density fluctuations occurring near the critical region are not explicitly taken into account. Since we are not interested in the critical region, this fact does not affect the performance of the soft-SAFT EoS in this work.

As previously done for the *n*-alkanes and perfluoroalkanes series,^{11,17} the soft-SAFT parameters can also be correlated with the molecular weight (M_w) of the

Table 1. Molecular Parameters for the Compounds Used through This Work Found by Fitting with Experimental Data

molecule	T range (K)	m	σ (Å)	ϵ/k_B (K)	ϵ_{HB}/k_B (K)	k_{HB} (Å ³)	Q (C m ²)	AAD (%)	ref
EG	270.0–470.0	1.751	3.668	326.05	4384	4195		1.13	41
DEG	280.0–475.0	2.548	3.860	334.40	4384	4195		2.74	41
TEG	300.0–610.0	3.190	4.010	340.58	4384	4195		4.18	41
TeEG	310.0–415.0	4.041	4.033	342.49	4384	4195		1.44	41
carbon dioxide	228.0–304.0	1.571	3.184	160.19			4.4×10^{-40}	1.00	34
nitrogen	71.0–125.0	1.205	3.384	89.16			1.2×10^{-40}	0.80	34
benzene	279.0–552.0	2.048	3.970	306.1			9.8×10^{-40}	2.70	34

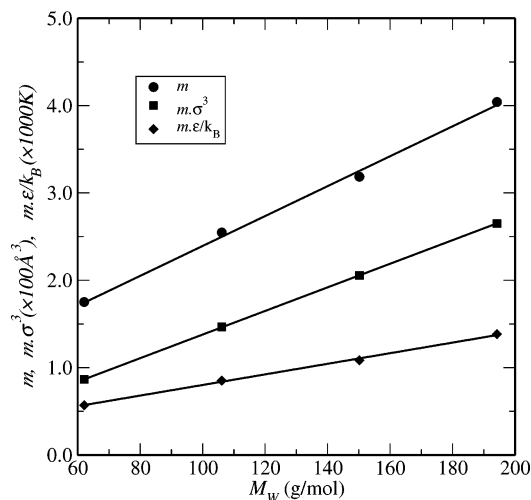


Figure 3. Graphical representation of the correlation of molecular parameters m , $m\sigma^3$, and $m\epsilon/k_B$ found for the EG oligomers (eq 14). See text for details.

oligomers of ethylene glycol. These correlations are expressed in the following set of equations

$$m = 0.698 + 0.017M_w \quad (14a)$$

$$m\sigma^3 = 2.804 + 1.351M_w \quad (14b)$$

$$m\epsilon/k_B = 195.8 + 6.064M_w \quad (14c)$$

Units of σ and ϵ/k_B are \AA and K, respectively.

A graphical representation of eq 14 is provided along with the optimized parameters in Figure 3. The correlation coefficient for all curves is higher than 0.99, providing an excellent correlation for extrapolation purposes. An advantage of having parameters with physical meaning is that their physical trend can be investigated, not just the correlation.¹¹ Note that when the linear correlation with the molecular weight is done the fluctuations of the parameters may be hidden by the multiplication by m and also by having σ^3 instead of σ . Although the molecular parameters are *effective* and we are using a crude model in which different groups are represented with the same σ and ϵ parameters, it is expected that they tend to a constant value, since the effect of the end groups (associating ones) should become smaller compared to the rest of the chain as the chain length increases. A detailed discussion on the subject can be found in ref 11. Although not shown here for conciseness, we have observed that m , σ , and ϵ follow the expected behavior. For instance, the values of m and ϵ are greater than in the corresponding alkanol, with the same number of CH_2 groups, comprising the specific interactions of the ether oxygen inside the molecule.

Since we are modeling EG oligomers in mixtures we also need the molecular parameters for the other components. The molecular parameters for methane, propane, and *n*-hexane were taken from our previous work.¹¹ No molecular parameters were previously fitted with the soft-SAFT equation for N_2 , benzene, and CO_2 with quadrupole interactions; they have been obtained within the present work with the molecular model outlined in the previous section and fitting to the available VLE data. The values for the quadrupole moments Q for these molecules obtained from the fitting are in agreement with the ones present in the litera-

ture.^{42,43} The carbon dioxide molecule is modeled as three segments, one of which has the quadrupole ($x_p = 1/3$), the nitrogen is modeled as being composed by two segments and one has the quadrupole ($x_p = 1/2$), and finally benzene is modeled as a set of six segments in a radial disposition and the quadrupole is assumed to be present in one of these segments ($x_p = 1/6$). The molecular parameters estimated are also reported in Table 1.

3.2. Mixtures. Once the molecular parameters of the pure components are available, soft-SAFT can be used to study the behavior of their mixtures. We present here the performance of the soft-SAFT equation for some mixtures of oligomers with other compounds. A comparison with G^E models for two chosen systems is reported, one with TEG and the other with TeEG. The solutes chosen were *n*-hexane and benzene. This choice was based on the experimental systems available, and although they present similar interactions (one associating fluid mixed with one which is not), their behavior in terms of VLE is quite different as it will be discussed later.

The data for mixtures of ethylene glycols with non-associating components are very scarce in the open literature. Only a few systems could be found. In fact, as we have mentioned in the Introduction, to our knowledge, this is the first time a systematic study of the solubility of different compounds on EG and its oligomers is performed. The experimental measurements found for the mixtures of the glycols investigated here come in various formats; that is, they are published as isobars, isotherms, or isopleths. A great advantage of using a molecular-based equation is that, once the molecular parameters of the pure compounds and the binary parameters at some selected conditions are fitted, the equation permits to perform a fair comparison of the different compounds *at the same thermodynamic conditions* as well as the influence of the molecular architecture in the phase behavior of the mixtures.

Throughout this work we have decided to use only one binary parameter for the soft-SAFT equation and for the PR equation, for all mixtures investigated. This is fair in terms of accounting for deviations from the ideal behavior with just one parameter, but it would provide values with greater deviations from unity than in the case where two binary parameters, separating size and energy deviations, are explicitly considered. The chosen parameter has been that related to the energy of interaction (ξ and ζ , respectively).

3.2.1. Mixtures of EG. The mixtures under study are three: EG with carbon dioxide, nitrogen, and methane. The experimental data for these mixtures have been taken from ref 36. Results obtained from soft-SAFT are displayed as full lines in Figures 4, 5, and 6, respectively, along with the experimental data (symbols). We have obtained the binary parameter at one temperature and use the soft-SAFT in a predictive manner for the other temperatures presented in these figures. The values of the binary interaction parameters were obtained at the lowest temperature, 323.15 K, for the mixtures of EG with carbon dioxide ($\xi = 0.8321$), with nitrogen ($\xi = 0.5188$), and with methane ($\xi = 0.6665$). Figures 4–6a also show predictions obtained with the soft-SAFT EoS if no binary parameters are used. Large deviations from the experimental data are observed in all cases for pure component predictions. This is due to the high asymmetry of the systems, but it also shows

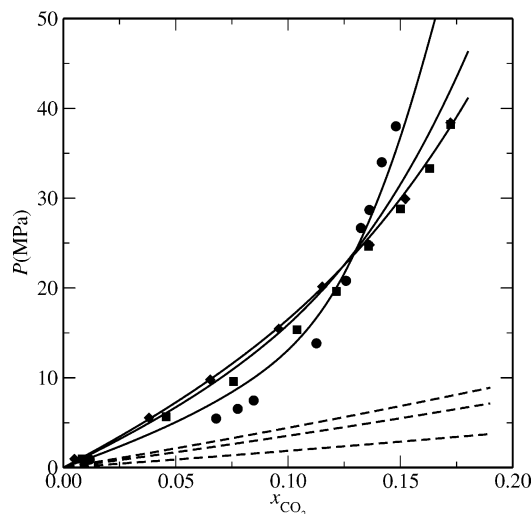


Figure 4. Isotherms for the mixture of ethylene glycol with carbon dioxide. Full line, soft-SAFT with one adjusted binary parameter; dashed line, soft-SAFT predictions without binary parameters. Symbols represent experimental data from ref 36 at different temperatures: circles (323.15 K), squares (373.15 K), and diamonds (398.15 K).

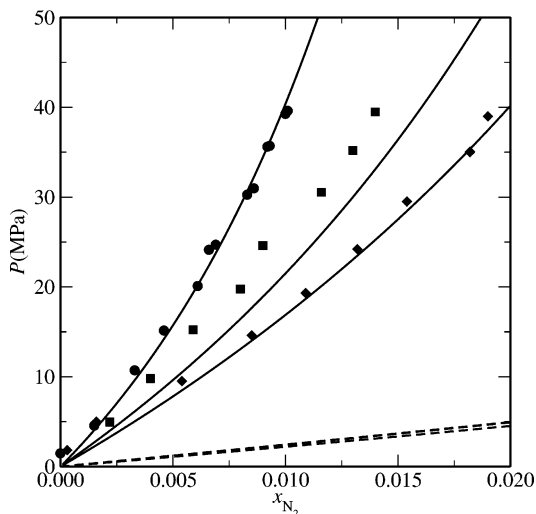


Figure 5. Isotherms for the mixture of EG with nitrogen (legend as in Figure 4).

how good the soft-SAFT model behaves when using just one temperature independent binary interaction parameter. The overall performance of the soft-SAFT equation for all three mixtures is quite good. Regarding the behavior of the three mixtures considered, the solubility decreases from CO₂ (most soluble) to nitrogen and methane, which requires higher pressures at the same temperature to be dissolved in EG. A similar behavior was observed by Wiestmet et al.⁴⁴ for mixtures with PEG and CO₂, nitrogen, and propane. For the EG/CO₂ mixture, soft-SAFT is able to capture the change in the solubility behavior of CO₂ in EG with pressure at the three temperatures considered.

We have focused on the mixture EG with methane to compare the performance of the two equations of state models used in this work. For this system, a study with G^E -based models cannot be made as the pressure is very high, i.e., far from the applicability of these models, which are valid only at pressures close to atmospheric. The study with PR EoS and its performance is compared with soft-SAFT's in parts a and b of Figure 6. Two comparisons are made: in the first case, the binary

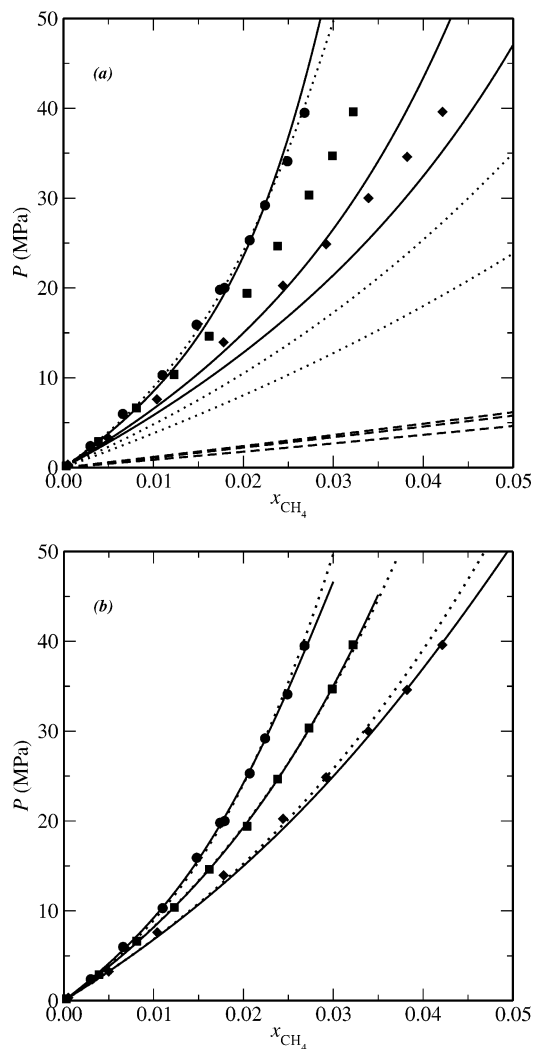


Figure 6. Isotherms for the mixture of EG with methane using PR and soft-SAFT EoSs. (a) Dashed lines, soft-SAFT predictions without binary parameters; full lines, soft-SAFT with one binary parameter ($\xi = 0.6665$); dotted line, PR with one fitted binary parameter ($\zeta_{ij} = 1.0109$); both fitted to $T = 323.15$ K. (b) Performance of the soft-SAFT (full lines) and PR (dotted lines) EoSs when the binary parameter is fitted as a function of temperature. Symbols as in Figure 4.

Table 2. Binary Parameters for the Soft-SAFT and PR EoS for the Ethylene Glycol + Methane Mixture for Each Temperature (Figure 6b)

T	ξ	ζ_{ij}
323.15	0.6665	1.0109
373.15	0.6344	0.9228
398.15	0.6426	0.8968

interaction parameter of both EoSs is kept *independent of temperature* ($\xi = 0.6665$ for soft-SAFT and $\zeta_{ij} = 1.0109$ for PR), fitted at 323.15 K (Figure 6a), while in the second case the binary parameter is fitted for each temperature (Figure 6b). The temperature-dependent parameters used in Figure 6b are presented in Table 2. Note that for this particular case the binary parameter in the soft-SAFT equation deviates considerably more from unity than the corresponding value in the PR EoS. However, the soft-SAFT parameter shows less dependence with temperature than the PR one. As expected, both equations perform well if the binary parameters are fitted at each temperature (Figure 6b), but in this case both models lose their extrapolative power.

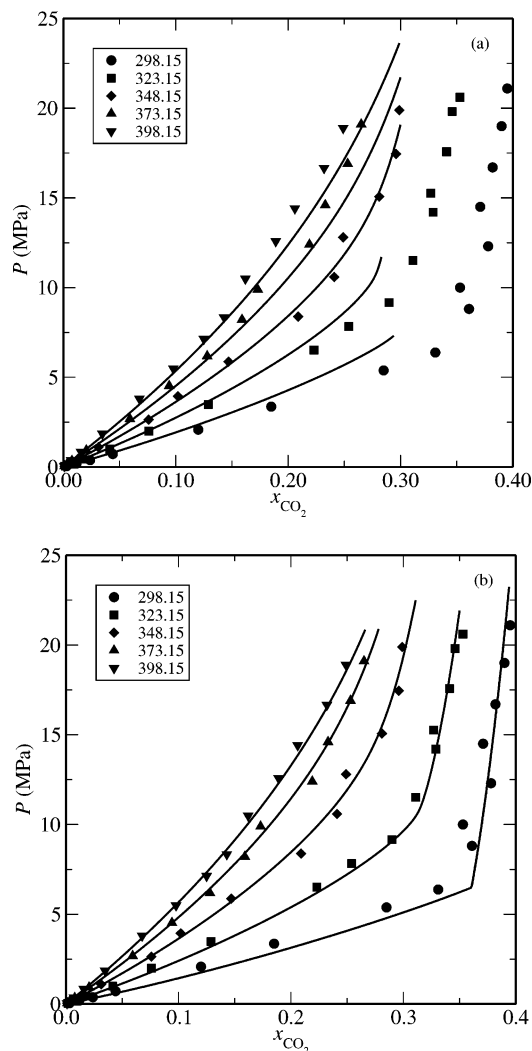


Figure 7. The DEG/CO₂ binary mixture. (a) Single binary parameter $\xi = 0.8935$, and (b) a binary parameter for each temperature (Table 3). Lines, soft-SAFT model; symbols, data from literature.³⁷

Table 3. Soft-SAFT Binary Parameters Used in Figure 7b

T (K)	298.15	323.15	348.15	373.15	398.15
ξ	0.9237	0.9085	0.8935	0.8852	0.8857

3.2.2. Mixtures of DEG. Only one mixture of DEG with carbon dioxide was found in the literature.³⁷ The performance of the soft-SAFT equation with the molecular model described before is shown in Figure 7. As in the previous case, the quadrupole interactions in the CO₂ molecules have been explicitly considered. Figure 7a depicts the performance of the soft-SAFT equation when the binary parameter is fitted to the intermediate temperature (348.15 K) and used to predict the behavior of the mixture at different temperatures. Although the equation is able to capture the behavior of the mixture in all cases, predictions deteriorate as one deviates from the fitted temperature and also as the molar fraction of carbon dioxide increases. The performance of the equation can be improved if the binary parameters are fitted to each temperature, as shown in Figure 7b. The temperature-dependent parameter values for Figure 7b are provided in Table 3. Note that the dependence of this parameter on temperature is very weak, and it seems to reach an asymptotic value at high temperatures. This limiting value could be used to predict the

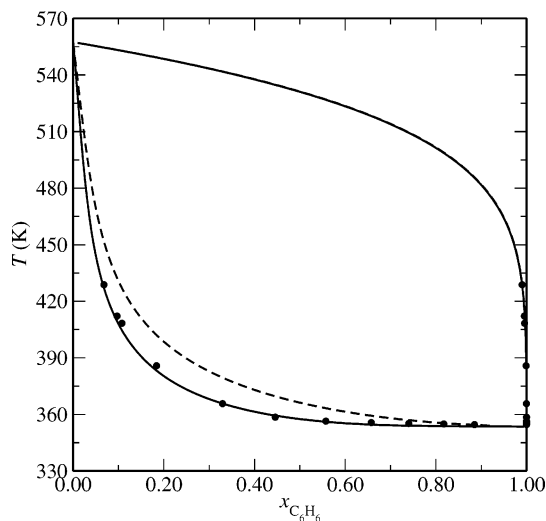


Figure 8. Isobaric phase diagram for the TEG/benzene mixture. Full line, soft-SAFT predictions with quadrupolar interactions included; dashed line, predictions from the original soft-SAFT equation. See text for details. Symbols represent data from literature.¹

behavior of the mixture at different temperatures, without further fitting.

It should be emphasized that this is a very challenging mixture, not only for the components integrating it but also for the thermodynamics conditions at which the system is investigated. The equation performs very well under these conditions (especially when a temperature-dependent binary parameter is considered), being able to detect a possible phase split at 298.15 K and an approximate pressure of 6 MPa. Although this phase split was not mentioned in the original article from which the data was taken, it is possible, since it may occur at temperatures below (and nearby) the critical temperature of CO₂. In fact, the equation follows the trend the experimental data presents at high pressures and low temperatures as well.

3.2.3. Mixtures of TEG. Mixtures of TEG/benzene¹ and TEG/*n*-hexane³⁸ were found in the literature and modeled with the soft-SAFT EoS. The mixture of TEG with benzene is rather symmetrical, and hence most models should describe it properly. The experimental T,x phase diagram at 0.1 MPa taken from the literature¹ is plotted together with the soft-SAFT model in Figure 8. For this system the binary interaction parameter was not necessary when the quadrupole interactions are explicitly considered, since agreement with the experimental data is excellent. As a reference, the results obtained without the inclusion of the quadrupole are also shown in Figure 8; in this case, a binary parameter would be needed to obtain the same accuracy as the one obtained with the quadrupolar term.

In concern of the mixture of TEG with *n*-hexane at 473 K, there is an important difference when the binary parameter is adjusted, as shown in Figure 9a with the (black) full lines. The binary parameter used in this case was $\xi = 0.9690$. This system is also studied with the PR equation, with $\zeta_{ij} = 0.9220$. The results are shown in Figure 9a in (red) full line. The dashed line corresponds to predictions from pure-component parameters for both soft-SAFT (black dashed line) and PR (red dashed line) EoSs. It can be observed in the figure that a possible third phase forms at high composition of *n*-hexane, as the experimental data seems to flatten out for hexane mole fractions above 0.3. In this region, the

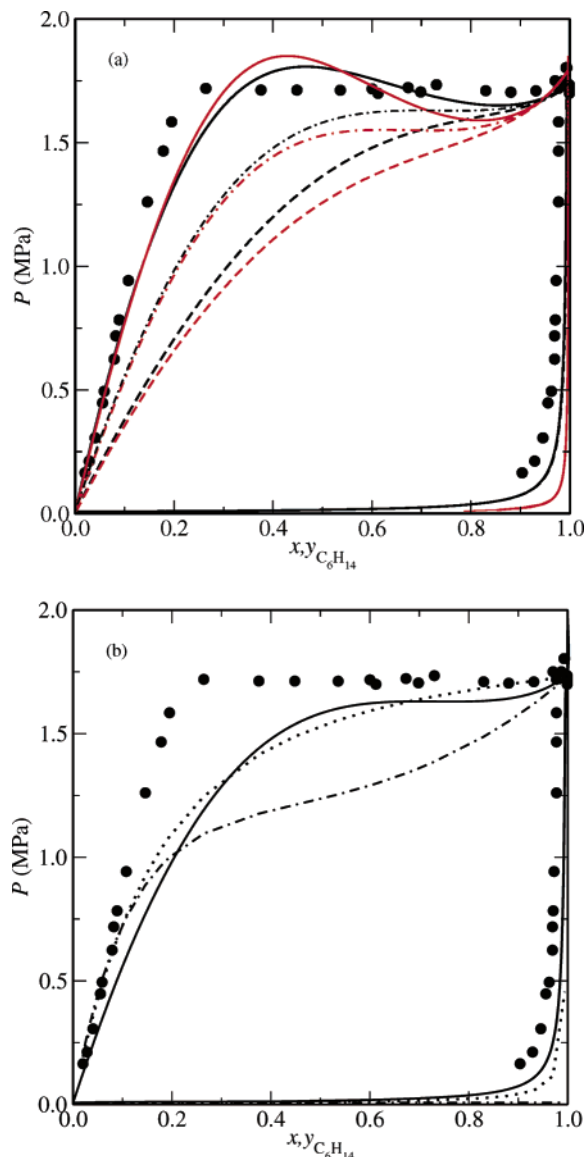


Figure 9. Isothermal vapor liquid equilibrium of the mixture of TEG with hexane ($T = 473.15$ K). (a) Black color represents soft-SAFT, and red lines represent PR. Full lines and dashed lines represent both EoSs with and without fitted binary parameters, respectively, and the dashed-dotted line represents both models fitted to the limit of stability. (b) Full line, soft-SAFT in the stability limit; dotted lines, sUNIQUAC; dashed-dotted, FH model. Symbols represent data from literature.³⁸

EoS models show phase instability and this is a very common situation when fitting a model to alkane/alcohol experimental systems.⁴⁵ The problem can be solved by fitting the binary parameters with the constraint of stability, given by the following stability function (SF)

$$SF = \frac{\partial \ln f_1^L}{\partial x_1} > 0 \quad (15)$$

which has been described in the literature.⁴⁶ Here f_1^L stands for the fugacity of the liquid phase and x_1 for the liquid composition of component 1. The binary parameter found using this procedure was $\xi = 0.9429$, for the soft-SAFT (black dashed-dotted line), and $\zeta_{ij} = 0.9560$ for the PR (red dashed-dotted line), very close to each other and not too far from the unity value. Results are shown in Figure 9a. In this case, the phase instability cannot be avoided without having a large

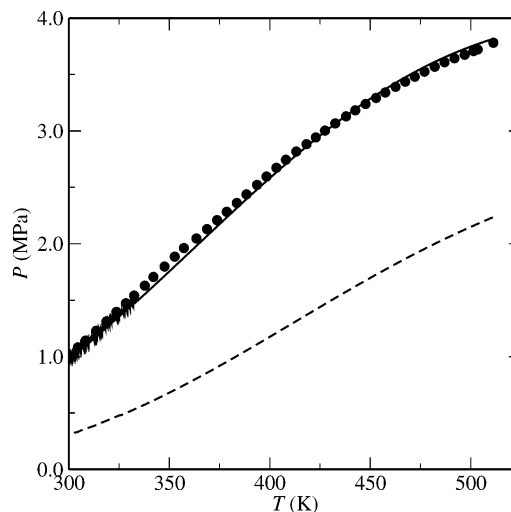


Figure 10. Mixture of TeEG and carbon dioxide at a fixed composition of CO_2 of 0.08. Full lines and dashed lines are soft-SAFT with and without a binary parameter, respectively, and symbols represent data from literature.³⁹

deviation from the experimental data. It should also be noticed that in all cases the performance of the PR EoS is somewhat worse than soft-SAFT's, especially in the region of binary parameters where model instability is present.

Figure 9b shows the study carried out with the G^E models for the TEG/*n*-hexane mixture. As in the soft-SAFT equation, the binary parameters for the two models were obtained by fitting to these data. For the sUNIQUAC model the *two binary parameters* values were $a_{12} = 1.08$ J/mol and $a_{21} = -0.08$ J/mol, while the fitted value for the FH model was $\chi = 1.905$. It possible to see that models studied (sUNIQUAC and Flory Huggins) show no tendency to have instability with the fitted parameters, but they also show a great deviation from experimental data compared to soft-SAFT, especially the FH model which clearly has a wrong tendency.

3.2.4. Mixtures of TeEG. The experimental data for the TeEG/carbon dioxide³⁹ mixture are the only ones presented in the form of isopleths in the original article. In this case the composition of carbon dioxide in the liquid phase was kept constant, and it was equal to 0.08. Figure 10 shows the soft-SAFT results when modeling this system with and without the binary interaction parameter. As in some of the previous mixtures, the pure-component parameters are able to qualitatively capture the shape of the curve, but if one is interested in quantitative results the binary parameter is needed. The binary interaction parameter found was $\xi = 0.8980$. Once again, a small change (about 12%) in the binary interaction parameter produces a relevant change in the model behavior, in the order of 40%.

As for the case of TEG, predictions with soft-SAFT for the mixture of TeEG with benzene⁴⁰ at 0.1 MPa show almost no deviations to the experimental data. This can be explained by the symmetry of these systems compared to the ones where a gas such as carbon dioxide or nitrogen is present. Figure 11a presents predictions obtained with the (polar) soft-SAFT and the results obtained with the PR EoSs with ($\zeta_{ij} = 0.9402$) and without the binary interaction parameter. Figure 11b shows how G^E -based models compare with soft-SAFT for this mixture. In this case, all models perform reasonably well since this is a system with no asymmetries. Both equations of state, soft-SAFT and PR,

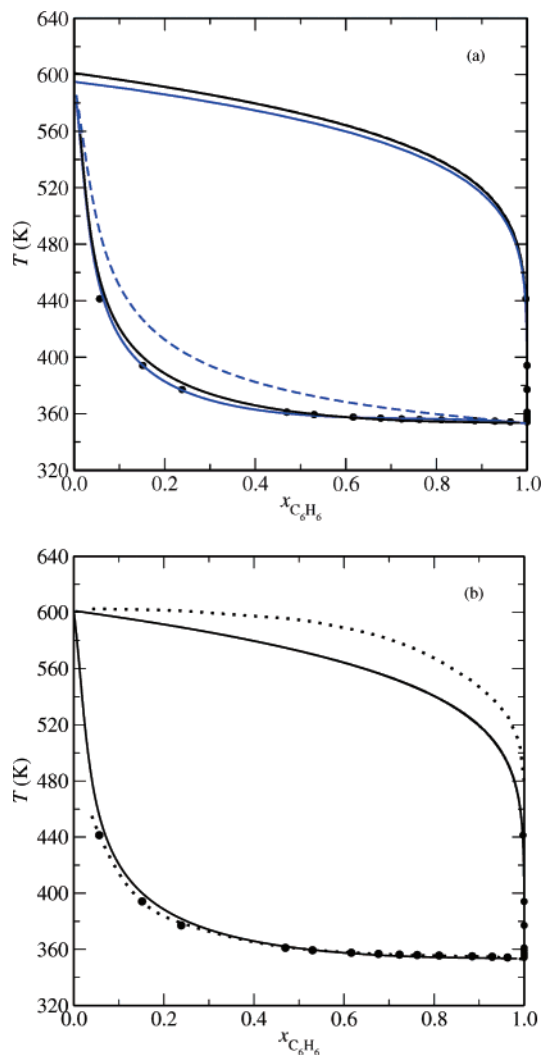


Figure 11. Description of the TeEG/benzene mixture at 0.1 Mpa. (a) Blue dashed line, predictions from PR; full line, quadrupolar soft-SAFT predictions; blue full line, PR with a binary parameter. (b) Full line, quadrupolar soft-SAFT predictions; dotted line, sUNQUAC with two binary parameters. Symbols represent experimental data from literature.⁴⁰

perform similarly, with or without the binary interaction parameter.

The G^E model (sUNQUAC, $a_{12} = 1.93$ J/mol, $a_{21} = 0.250$ J/mol) also performs well for the liquid compositions (its parameters were adjusted to these data), but there is some overprediction of the bubble-point temperature: about 5% from the values given by PR and soft-SAFT. Note, however, that for this system there is no available data for lower compositions of benzene, only a few data points for higher compositions; hence, the vapor phase predictions should be taken with caution.

4. Influence of the Molecular Architecture on the Solubility

So far we have performed a systematic check on the description of EG oligomers mixtures with the soft-SAFT EoS as well as with other thermodynamic models. Soft-SAFT has proved to be accurate and with good extrapolative power with one temperature independent parameter in most of the cases. The next step is to use the equation to check the influence of the molecular architecture on the solubility of different compounds in EG oligomers, in particular, the influence of the chain

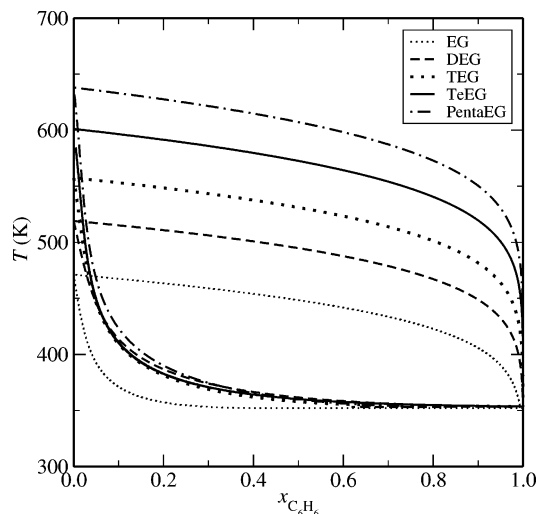


Figure 12. The influence of the chain length on the solubility of benzene in EG, DEG, TEG, and TeEG at 0.1 Mpa, as obtained from the soft-SAFT model.

length and the effect of breaking (or not) hydrogen bonds when solubilizing nonassociating compounds in them.

4.1. EG, DEG, TEG, TeEG, and Pentaethylene Glycol (PentaEG) in Benzene. It is of great interest to check the soft-SAFT predictive capability of the VLE for other mixtures. Hence, a VLE prediction of the system EG/benzene, DEG/benzene, and PentaEG/benzene at 0.1 Mpa is made here for comparative purposes. Calculations are performed with the molecular parameters of the pure components; based on the results presented, no binary parameters are needed for these mixtures.

Soft-SAFT EoS predictions showing the effect of the chain length on the solubility of EG, DEG, TEG, TeEG, and PentaEG on benzene at 0.1 Mpa are shown in Figure 12. It is worth noting that, while the dew points are strongly dependent on chain length, the boiling points seem to be independent of the chain length, except for the EG/benzene mixture. Note also that the differences in the dew points show an almost constant increase with chain length, a direct consequence of the increase vapor pressure value of the pure components with chain length.

4.2. EG, DEG, TEG, TeEG, and PentaEG in Carbon Dioxide. Finally, soft-SAFT is also used to study the influence of the chain length on the solubility of carbon dioxide in the EG oligomers (from EG to PentaEG). The molecular parameters for PentaEG have been obtained from eq 14. The binary parameter for all mixtures was set to 0.88. This value lies between those fitted to the EG and TeEG mixtures with CO_2 , and it is also very close to the limiting value of the temperature-dependent parameter for the DEG/ CO_2 mixtures.

Figure 13 shows how the influence of the molecular architecture (chain length) is remarkable in this case; the solubility increases as the chain length increases, and changes are quite more significant for the shorter molecules. This may be explained by the fact that EG and DEG need to break hydrogen bonds to solubilize CO_2 ; as the chain length increases the solubility is achieved without hydrogen-bond breaking, being favored by the van der Waals interactions between the alkyl groups inside the chain and the CO_2 molecules. The ability to accommodate the CO_2 molecule within the non-hydrogen-bonding part of the molecule explains

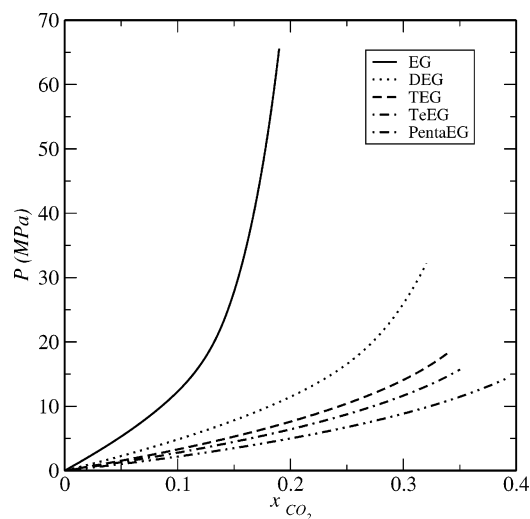


Figure 13. The influence of the chain length on the solubility of carbon dioxide in EG, DEG, TEG, TeEG, and PentaEG as predicted from the soft-SAFT EoS at 373.15 K.

why the differences in solubility of CO_2 become smaller as the chain length of the EG oligomers increases. Wiesmet et al.⁴⁴ have also observed a similar effect, although less noticeable: they measured the influence of the molecular weight of PEG on solubilizing CO_2 , obtaining a different behavior for the lightest compound, and no influence of chain length for the rest of the polymers investigated. The deviations were attributed to the influence of the chain ends in the shortest polymer, although it was not quantified.

Conclusions

We have developed a molecular model for the EG oligomer series within the context of the soft-SAFT approach. Molecular parameters were obtained by fitting to available experimental data for the VLE of pure components, ranging from EG to TeEG. It was possible to propose a correlation of the chain length, size, and energy of interaction parameters with the molecular weight of the compounds, while the association parameters were fixed in all cases. This provides transferable parameters for the series and also for longer molecules, such as PEG. The quadrupolar interactions have been explicitly considered for the cases of CO_2 , nitrogen, and benzene. Although this has no effect on the pure-component description, the inclusion of this interaction remarkably improves the description of the mixtures.

The use of the soft-SAFT equation allows a systematic study of the influence of different variables (chain length and thermodynamic conditions) on the solubility of several compounds in ethylene glycols. We have used available experimental data of some mixtures to fit one binary parameter of the soft-SAFT EoS to a given temperature and use this parameter in a predictive manner for the rest of the temperatures. It has also been shown that a temperature-dependent parameter improves the description in some cases. Once all needed parameters were obtained, soft-SAFT permits the study of the influence of the chain length on mixtures of EG oligomers with other compounds, at the same temperature and/or pressure. We have observed that when solubilizing a liquidlike solvent (benzene) the influence of the chain length is more noticeable in the dew point, while almost no effect is observed in the boiling point, except for the shortest member of the series, EG. On the contrary, the solubility of carbon dioxide on these

oligomers strongly depends on chain length, since the breaking of hydrogen bonds in the EG and DEG is clearly harder for these oligomers.

Finally, the performance of the soft-SAFT equation for two compounds and two oligomers has been compared with other well-established thermodynamic models: G^E -based models and the PR equation. G^E models are as accurate as the rest of the models employed here for the TeEG/benzene mixture, but for the TEG/*n*-hexane mixture the FH model shows some difficulties in describing this system in a sound manner. Soft-SAFT provides better predictions than PR with a temperature-independent binary parameter, while both models perform similarly if a temperature-dependent binary parameter is used. This acts in favor of the extrapolative power of a molecular-based EoS vs most traditional equations.

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Nomenclature

A = Helmholtz energy
 a = temperature-independent binary parameters in the sUNQUAC model
 g = radial distribution function
 m = chain length, number of LJ segments (except in eq 10, $m = f(\omega)$)
 M_w = molecular weight
 Q = quadrupole moment ($\text{C}\cdot\text{m}^2$)
 R = real gas constant
 T = temperature
 x = molar fraction
 X = fraction of molecules not bonded to a certain site

Greek Symbols

χ = Flory parameter
 ϵ = soft-SAFT LJ energy parameter
 η = soft-SAFT binary interaction parameter for size
 ξ = soft-SAFT binary interaction parameter for energy
 σ = soft-SAFT LJ size parameter (segments diameter)
 τ = energy parameter of the sUNQUAC model
 ϕ = volume fraction
 ω = eccentric factor

Superscripts

assoc = related to association contributions
 chain = related to chain bonding contributions
 ideal = related with the ideal gas contribution
 polar = related to polar moments (di- or quadrupolar) contributions
 ref = reference term contributions
 total = total sum of the contributions
 α = site of association

Subscripts

c = critical property
 HB = association related
 i = component i
 j = component j
 LJ = Lennard-Jones
 r = reduced property

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