

Modeling the Phase Equilibria of Poly(ethylene glycol) Binary Mixtures with soft-SAFT EoS

Nuno Pedrosa,[†] Lourdes F. Vega,[‡] João A. P. Coutinho,[†] and Isabel M. Marrucho^{*†}

CICECO, Departamento de Química, Universidade de Aveiro, 3810-193 Aveiro, Portugal, and Institut de Ciència de Materials de Barcelona (ICMAB–CSIC), Consejo Superior de Investigaciones Científicas, Campus de la U.A.B., 08193 Barcelona, Spain

The present work addresses the modeling of the phase equilibria of several poly(ethylene glycol) mixtures, with different types of solvents, by the soft-SAFT (statistical associating fluid theory) equation of state (EoS). The molecular parameters for poly(ethylene glycol) were obtained as a function of the molecular weight by extrapolation from the first four members of the ethylene glycols series, up to tetraethylene glycol, obtained in a previous work [Pedrosa et al. *Ind. Eng. Chem. Res.* 2005, 44, 7027]. The parameters for the different solvents were either taken from previous works or fitted for the first time to available vapor–liquid equilibrium data within the soft-SAFT during this work. Their quadrupolar nature was explicitly taken into account. The phase equilibria studied concerns the solubility of gases, such as nitrogen and propane, and vapor–liquid equilibria with both nonassociating solvents, such as benzene, and associating solvents, such as methanol, ethanol, and water. The liquid–liquid equilibria of poly(ethylene glycol) with different solvents, namely, toluene, ethylbenzene, *n*-propylbenzene, and *tert*-butyl acetate, were also described using the soft-SAFT EoS. soft-SAFT was able to provide an overall good description of all mixtures investigated here. The advantages and shortcomings of the model as well as its capability to describe the dependence of the phase equilibria with the molecular weight of the polymer are discussed.

Introduction

Poly(ethylene glycol), along with poly(ethylene oxide), belongs to a family of polymers that exhibit very different thermodynamic properties according to the molecular weight. The low molecular weight members are viscous fluids or waxy solids, while the high molecular weight ones are crystalline thermoplastics. This difference in behavior is mainly due to the importance of the hydroxyl end groups in the polymeric chain. Poly(ethylene glycol) is well-known for its hydrophilicity, water solubility, lack of toxicity, and excellent biocompatibility. It has been combined physically or chemically with many therapeutic polymeric systems, either proteins and particles or implants, to make them stealthy with respect to natural body defenses.^{1–3} It is also used in other fields such as in agriculture, wood processing, and the paint industry, where it has an emulsifying role, and in batteries, chromatography, and medicine, as a supporting agent.⁴

Although poly(ethylene glycol) (PEG) is found in a wide range of applications, the modeling of PEG mixtures phase equilibria still remains a challenging task because of its associating behavior and also the change in the polymer thermophysical properties with the molecular weight. Today we attend to an increasing complexity of the polymer systems resulting from the development of new processes at extreme conditions (as, for example, those where one of the components is supercritical) and/or the design of new materials for a specific need, where polymer architecture plays a dominant role. From a past situation where polymers were used in an almost pure state to the present situation where the polymeric material properties can be tailored to specification by formulation, polymer phase equilibria have increased in complexity but also

in importance. Because of the large differences in the molecular sizes of polymer and solvents, the polydispersity of polymers, and the relative importance of the different groups within the polymers according to the polymer molecular weight, the phase behavior of polymer systems is usually more complex and rich than that of systems of small molecules. The development of improved thermodynamic models for polymer systems and the evaluation of the performance and robustness of these models is, thus, a stringent requirement.

One model of rising popularity, because of its accuracy in the estimation of thermodynamic properties of polymer solutions, is the statistical associating fluid theory (SAFT).⁵ SAFT is a modeling approach in which an equation of state (EoS) is expressed as a summation of the various microscopic contributions present in the system to the residual Helmholtz energy (A^{res}). It has been shown that the separation of the different molecular contributions, through the introduction of different mathematical terms, leads to a better and more fundamental description of the phenomena under consideration at the molecular level. The SAFT EoS was originally developed by Chapman et al.⁵ using the first-order thermodynamic perturbation theory (TPT1) due to Wertheim.^{6–9} Since then, a number of different versions of this equation were reported in the literature. The major difference between the various versions is the reference fluid adopted. In the original version of Chapman, the adopted reference fluid is the hard-sphere fluid; in soft-SAFT, developed by Blas and Vega,^{10,11} it is the Lennard-Jones fluid; in SAFT-VR, by Gil-Villegas et al.,¹² it is the square-well fluid with a variable range; while in PC-SAFT, proposed by Gross and Sadowski,¹³ the reference fluid used is the hard-chain fluid. All of them use Wertheim's TPT1 for the association contributions to the phase equilibria.

The SAFT EoS have been previously used to describe the phase behavior of several systems involving polymers^{14–17} ranging from liquid–liquid, vapor–liquid to gas–liquid equilibria. However, little attention has been paid to associating

* Corresponding author. E-mail: imarrucho@dq.ua.pt. Tel.: +351 234 401 406. Fax: +351 234 370 084.

[†] Universidade de Aveiro.

[‡] ICMAB–CSIC.

Table 1. Molecular Parameters of the Soft-SAFT EoS for Nonpolymer Compounds

compound	m	σ (Å)	ϵ/k_B (K)	Q ($\times 10^{-40}$ C m ²)	k_{HB} (Å ³)	ϵ_{HB}/k_B (K)	reference
carbon dioxide	1.571	3.184	160.19	4.40			20
nitrogen	1.205	3.384	89.16	1.20			20
propane	1.776	3.811	219.5				43
methanol	1.491	3.375	220.4		3213	4847	44
ethanol	1.740	3.635	234.8		3387	2641	44
2-propanol	2.003	3.831	224.9		3450	2250	this work: data from DIPPR ⁴⁵
water	1.000	3.190	408.5		2367	2707	46
benzene	2.048	3.970	306.1	9.80			20
<i>tert</i> -butyl acetate	3.209	3.815	261.84				this work: data from ref 45
toluene	2.374	4.013	305.2	9.80			this work: data from ref 45
ethylbenzene	2.644	4.061	307.1	9.80			this work: data from ref 45
<i>n</i> -propylbenzene	2.886	4.126	309.8	9.80			this work: data from ref 45

polymers. Kleiner et al.¹⁷ modeled the mixture of poly(ethene-*co*-acrylic acid) and poly(ethene-*co*-methacrylic acid) with their monomers, which are carboxylic acids, i.e., they tend to associate through the carboxylic group. Kouskoumvekaki et al.¹⁸ considered the ternary mixtures of polyamide-6 with ϵ -caprolactam and water, taking into account that all the association sites in the chain are able to form hydrogen bonds, i.e., the carbonyl groups and the end hydroxyl groups were modeled as association points. Wiesmet et al.¹⁹ modeled the solubility of nitrogen, propane, and carbon dioxide in poly(ethylene glycol), assuming that only the end hydroxyl groups were able to form hydrogen bonds. In all these cases, the PC-SAFT EoS was used.

This work is part of an ongoing project aimed to describe polymer phase equilibria using the soft-SAFT model.¹⁰ Our goal here is to check the performance of the soft-SAFT model for associating polymers. Poly(ethylene glycol) systems were chosen to illustrate it, since the phase behavior of poly(ethylene glycol) oligomers up to tetra(ethylene glycol) in several solvents using soft-SAFT was already addressed in a previous study.²⁰ Here, this study will be extended to higher molecular weight compounds using the correlation as a function of the molecular weight previously developed²⁰ and to a variety of solvents. The different mixtures investigated here show a rich phase equilibria behavior, usually of type IV or type V in the classification of Scott and van Konynenburg.²¹ These types of equilibria exhibit lower and higher critical end points because of the large differences in size and/or energy of interaction between the solvent and the polymer. In practical terms, this leads to liquid–liquid-phase equilibria exhibiting an upper critical solution temperature (UCST), mainly driven by the differences in energy, and/or a lower critical solution temperature (LCST) conditioned by the difference in size of the components.

Methodology and Model

The SAFT type of equations of state are usually written in terms of the residual Helmholtz energy,

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

where the superscripts “id”, “ref”, “chain”, “assoc”, and “polar” stand for ideal, reference, chain, association, and polar terms, respectively. The reference term is the EoS of the reference fluid, which can be a hard-sphere fluid with a dispersion term, a Lennard-Jones fluid, a hard-chain fluid, or a square-well fluid. The chain term is the residual energy contribution of the chaining of the segments, derived from Wertheim’s theory in the limit of full association and explicitly including the radial distribution function of the reference fluid. In molecules where some kind of association exists, i.e., a specific intermolecular interaction, which is stronger than the van der Waals interactions and highly directional, such as hydrogen bond formation, the

association term, derived from Wertheim’s theory, has to be added up. If a compound exhibits a quadrupolar moment, its effect in the phase equilibria description by the SAFT EoS may be accounted for in an explicit way by adding an additional polar term to eq 1. The same holds for dipolar and different multipolar terms. The detailed derivation of the polar term is given elsewhere.²² The magnitude of the quadrupole is accounted for with an additional parameter, Q , the quadrupolar moment.

The version of the SAFT EoS used throughout this work, soft-SAFT, uses a Lennard-Jones fluid as the reference fluid. This model was developed by Blas and Vega,¹⁰ and it has been extensively discussed in the literature.^{10,11,23–26} Each molecule in the SAFT approach is described by a set of three parameters: σ , which is the molecular size of each segment in the molecule, ϵ , its energy, and m , the parameter used to account for the number of segments describing a nonspherical molecule. Two additional parameters are used for associating molecules: k_{HB} , representing the volume occupied by the association site bonded to another associating molecule, and ϵ_{HB} , related to the energetic strength of the association. As stated, quadrupolar molecules have an additional parameter Q , the quadrupolar moment.

For some systems, the accurate description of mixture data is only possible if a binary interaction parameter is used, especially in the case of polymer systems. The binary interaction parameter accounts for the effect that differences in the size and/or dispersive energy of the molecules have on the free energy of the system. In the soft-SAFT EoS approach, two binary interaction parameters can be used, explicitly separating the two effects: η and ξ , accounting for differences in size and energy of the segments making up the chain and the solvent molecules, respectively. A value of unity means that no binary interaction parameter is used.

One of the most important issues related with the calculation of phase equilibria of polymer mixtures is the estimation of the molecular parameters of the equation of state for the pure polymer. The molecular parameters of the SAFT EoS are usually determined by fitting them to vapor pressure and saturation density data of the pure compounds. While this is a valid procedure for the majority of the low molecular weight substances, it is impossible to accomplish for pure polymers, since they do not have a measurable vapor pressure. There are two alternative techniques that can be used to estimate the molecular parameters for pure polymers: the use of a correlation of a series of low molecular weight compounds that is extrapolated to the molecular weight of the polymer or the fitting of the polymer molecular parameters directly to a binary mixture, along with the binary interaction parameter. The former has a limited application since few polymers can be related to a series of oligomers, while the later has the limitation that some

mixture data is included into the fitting. One polymer where the first approach was used is polyethylene,²⁷ since it can be related to the very well studied series of compounds, the *n*-alkane series. Another case that can be considered within this approach might be PTFE (polytetrafluoroethylene) using the soft-SAFT studies of the *n*-perfluoroalkanes series already performed.^{23,28} However, for the vast majority of the polymers, there is no series of oligomers such that their parameter can be correlated with the molecular weight, as, for example, in the case of polystyrene where data for oligomers is very scarce.²⁹

We have taken advantage of the fact that a correlation of the molecular parameters for the series of ethylene glycol oligomers has already been developed in a previous work.²⁰ The first approach of obtaining the molecular parameters of poly(ethylene glycol) was used here. These correlations are used here to estimate the molecular parameters for the polymer in a transferable manner. The association scheme used assumes that only the end hydroxyl groups associate with other chains of polymer or solvent. This is in agreement with the work of Crupi et al.,³⁰ who studied the associating interactions present in pure liquid ethylene glycols (including several PEG polymers of low molecular weight) using Rayleigh wing and Fourier transform infrared (FTIR) spectroscopies. They concluded that, in liquid ethylene glycol, all the O–H groups are involved in the formation of hydrogen bonds. This behavior is similar to the one observed for *n*-alkanols, by the same authors.³⁰ It was also observed that intramolecular interactions in PEG of molecular weights of 200 and 2000 were of very low probability. This means that, for reasons of polymeric steric hindrance, these intramolecular interactions can be neglected when modeling PEG with soft-SAFT. In fact, the existence of ring associating structures cannot be modeled in the TPT1 context, as discussed in the reviews on SAFT.^{31,32} Accordingly, poly(ethylene glycol) is modeled here assuming that only the end hydroxyl groups are able to associate with other chains of the polymer or solvents. This has already proved to be a good assumption in the description of the solubility of gases in poly(ethylene glycol)¹⁹ and for the ethylene glycol oligomers previously studied.²⁷

Hence, the soft-SAFT description of poly(ethylene glycol) was accomplished by using the series of ethylene glycol oligomers. The molecular parameters correlation developed based on that series²⁰ is here reported for completeness: where

$$m = 0.698 + 0.017M_n \quad (2a)$$

$$m\sigma^3 = 2.804 + 1.351M_n \quad (2b)$$

$$m\epsilon/k_B = 195.8 + 6.064M_n \quad (2c)$$

M_n is the number molecular weight of the polymer. The units of σ and ϵ/k_B are Å and K, respectively.

The molecular parameters of the soft-SAFT EoS for the solvents used in this work were either taken from previous published works or fitted to available vapor–liquid equilibrium data if the solvents have not yet been modeled with soft-SAFT. In all cases, the molecular nature of the compounds (nonassociating, associating, quadrupolar terms, etc.) was taken into account explicitly. All the parameters used are provided in Table 1.

Results and Discussion

The data available for binary poly(ethylene glycol) mixtures is surprisingly scarce. The vapor–liquid equilibrium data focus essentially on the solubility of gaseous compounds such as nitrogen,¹⁹ propane,¹⁹ and carbon dioxide.^{19,33} Some data also

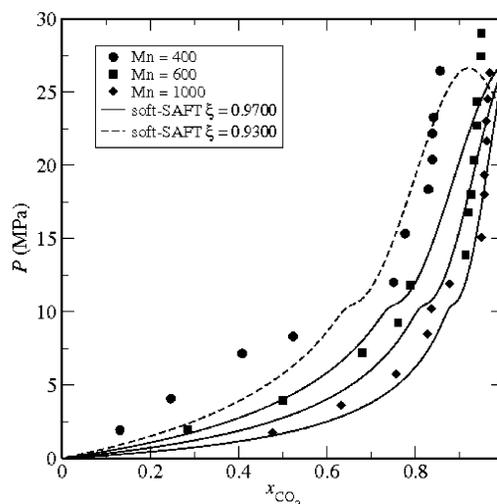


Figure 1. Phase equilibria description by the soft-SAFT EoS of the solubility of carbon dioxide in poly(ethylene glycol) of molecular weights 400, 600, and 1000 g/mol at 323.0 K. The experimental data was taken from Daneshvar et al.³³

exist on the solubility of associating lower alcohols such as methanol,³⁴ ethanol,³⁴ and 2-propanol³⁵ and water.³⁶ In the case of liquid–liquid-phase equilibria, data for poly(ethylene glycol)/*tert*-butyl acetate from Saeki et al.³⁷ and for mixtures with aromatics such as toluene, ethylbenzene, and *n*-propylbenzene were reported by Sabadini.⁴ Despite the limited data available, the resulting phase behavior is quite rich. In the next sections, we will attempt to describe the same behavior with the soft-SAFT model, trying to highlight the molecular interactions leading to the macroscopic behavior.

Vapor–Liquid Equilibria. The modeling of the solubility of carbon dioxide in PEG 400, 600, and 1000 g/mol, using the experimental data from Daneshvar et al.³³ at 323 K is displayed in Figure 1. According to the authors, the molecular weight distribution for the PEG used is quite narrow ($M_w/M_n = 1.05$). The polymer can, thus, be considered monodisperse. Note that, for this system, the carbon dioxide is close to or in the supercritical state. A binary interaction parameter close to unity was used ($\xi = 0.9700$) for all molecular weights. However, for the poly(ethylene glycol) with a molecular weight of 400 g/mol, this binary interaction parameter was not good enough to model the solubility of carbon dioxide in poly(ethylene glycol). As shown in Figure 1, a different binary interaction parameter was fitted to the solubility data for the polymer of 400 g/mol. The description of the phase equilibria by soft-SAFT presents a slight instability as the equation describes the transition of a liquid–vapor equilibria to a liquid–liquid equilibria with supercritical carbon dioxide. We have also modeled the phase equilibria for the mixture poly(ethylene glycol) 1500 g/mol of carbon dioxide from Wiesmet et al.¹⁹ and for the polymers of 400 and 600 g/mol at other temperature from Daneshvar et al.,³³ obtaining similar results to those presented in Figure 1. For the sake of shortness and clarity, these results are provided as Supporting Information.

The experimental solubility data from Wiesmet et al.¹⁹ of propane in poly(ethylene glycol) was also modeled using the soft-SAFT EoS. In the present case, the molecular weight of the polymer ranges from 200 to 8000 g/mol. The molecular weight of the polymers used by the authors has a polydispersity index (M_w/M_n) of 1.1; the polymer can, thus, be considered monodisperse. The results are displayed in Figure 2 for the polymers with molecular weight of 200 and 8000 g/mol. Excellent performance of the soft-SAFT model in the description

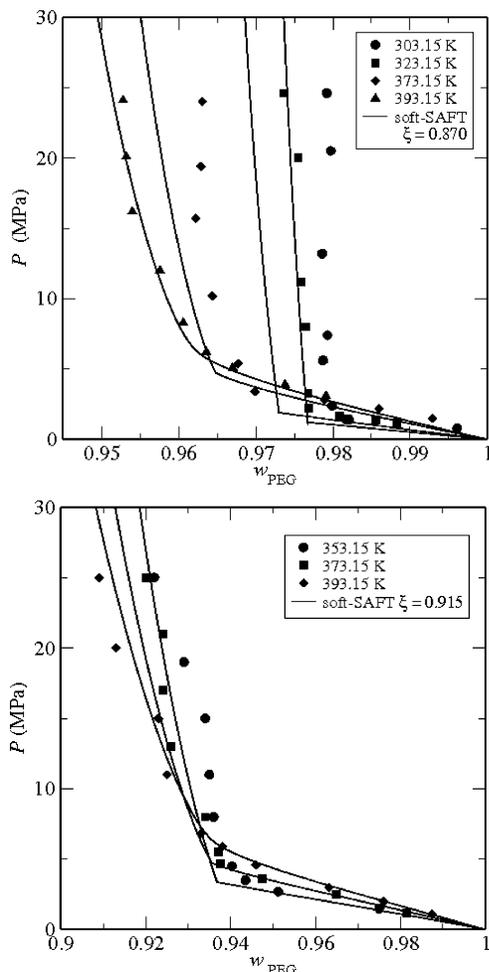


Figure 2. Solubility of propane in poly(ethylene glycol) at four different temperatures as described by the soft-SAFT EoS. Experimental data from Wiesmet et al.¹⁹ (a) poly(ethylene glycol) with a molecular weight of 200 g/mol and a soft-SAFT binary interaction parameter $\xi_{ij} = 0.870$; (b) poly(ethylene glycol) with a molecular weight of 8 000 g/mol and a soft-SAFT binary interaction parameter $\xi_{ij} = 0.915$.

of the temperature dependence of the equilibria, especially for temperatures higher than the critical temperature of propane, is observed. The same accuracy was obtained for polymers with molecular weights of 1500 and 4000, as shown in the results presented in the Supporting Information. A binary interaction parameter was required to describe the experimental data. The correction of this binary interaction parameter, ξ_{ij} , decreases in magnitude from PEG 200 with a value of 0.870 to PEG 8000 with a value of 0.915, closer to unity. This decrease in the correction with increasing molecular weight seems to indicate that the energetic crossed interaction decreases with the polymer molecular weight. There is a steep transition on the vapor–liquid-phase equilibria, similar to the case of carbon dioxide but having a greater importance in the case of propane. This behavior is due to the transition of a vapor–liquid equilibria to a liquid–liquid-phase equilibria diagram as the pressure increases. The soft-SAFT EoS accurately describes this behavior.

The solubility of the gaseous nitrogen in poly(ethylene glycol) is challenging to model with soft-SAFT, as shown in our previous work²⁰ for the vapor–liquid equilibria of nitrogen in ethylene glycol. This is a common problem with the nitrogen systems resulting from the large asymmetry in the enthalpic and entropic interactions displayed by these systems. The soft-SAFT description of the solubility of nitrogen in poly(ethylene glycol)s of molecular weights of 1500, 4000, and 8000 g/mol

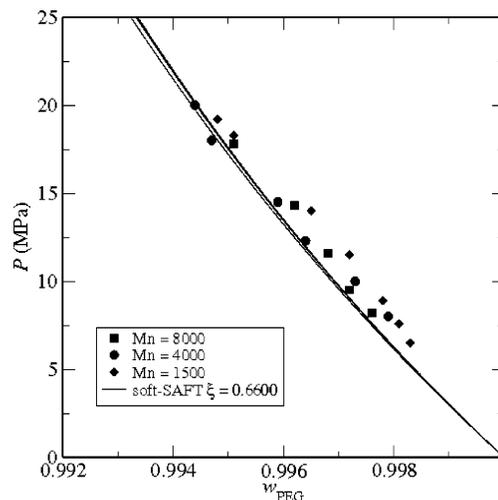


Figure 3. Modeling of the solubility of nitrogen in poly(ethylene glycol) with soft-SAFT. The molecular weights used range from 1 500 to 8 000 g/mol. The experimental data was taken from Wiesmet et al.¹⁹

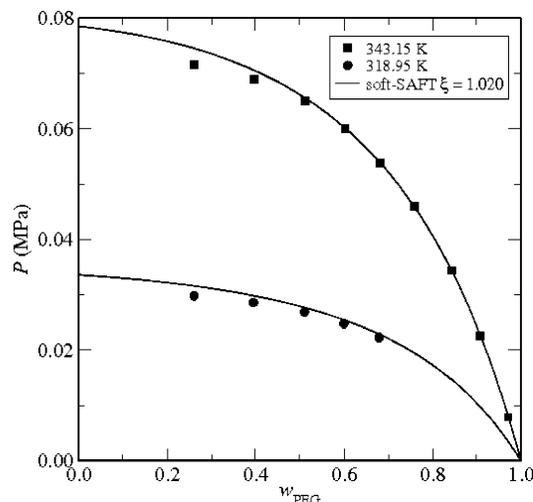


Figure 4. Vapor–liquid equilibria of the mixture poly(ethylene glycol)/benzene modeled by the soft-SAFT EoS. The experimental data is from Booth and Devoy.³⁸

at 353.15 K is reported in Figure 3. The experimental data used were taken from Wiesmet et al.¹⁹ In order to obtain an accurate correlation of the experimental data, the same binary interaction parameter was used for all molecular weights, since on these molecular weight values, the phase equilibria are not significantly affected by the polymer molecular weight. However, this value is not the same one used for the nitrogen/ethylene glycol binary mixture²⁰ changing from 0.5188 for ethylene glycol to 0.6600 to the poly(ethylene glycol) of 1500, 4000, and 8000 g/mol, in a similar manner as it was obtained for other gases. A systematic underprediction of the gas–liquid coexistence phase line for high polymer concentrations is observed.

In Figure 4, the soft-SAFT description of the vapor–liquid equilibria of benzene and poly(ethylene glycol)³⁸ with a molecular weight of 5700 g/mol and a polydispersity of 1.1, at 318.95 and 343.15 K, is shown. A binary interaction parameter slightly higher than $\xi = 1.020$ was used to accurately describe the phase behavior at both temperatures. The SAFT EoS is able to capture the dependency of the mixture activity with the temperature very accurately.

The previous examples dealt with gases/vapors that do not have association interactions with PEG. The interactions present in those mixtures only involve association between polymer

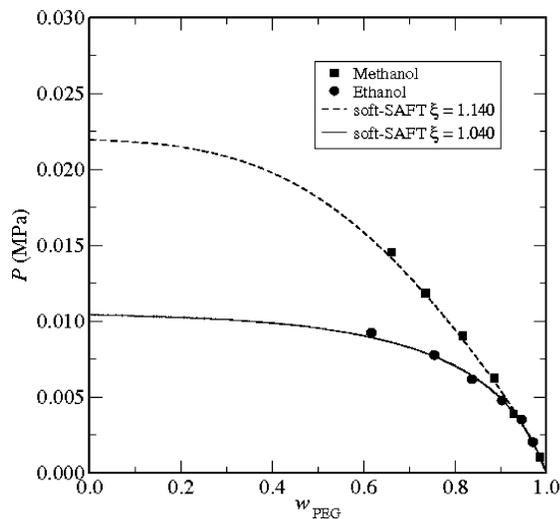


Figure 5. Modeling of the vapor–liquid equilibria for the mixtures poly(ethylene glycol)/ethanol and poly(ethylene glycol)/methanol at 303.15 K. The molecular weight of the poly(ethylene glycol) is 600 g/mol in both cases. The experimental data is from Kim et al.³⁴

chains. Mixtures of poly(ethylene glycol) and alkanols present a more complex web of interactions, since both the polymer and the alkanol molecules associate among themselves and also with the other components of the mixture, meaning that self-association and crossed association are present. This kind of association can be modeled within the SAFT-type EoSs using an analytical or a numerical approach. We have decided not to use the analytical form of the association term because it would result in a system of nonlinear equations for each case of the association behavior needed. Instead, the numerical approach developed by Tan et al.³⁹ was used to calculate the fraction of nonbonded molecules and, hence, the number of molecules in an associated state. In their work, an algorithm was developed to solve the problem of deriving a specific expression for the fraction of nonbonded molecules for each association model, making it a general procedure. At the same time, the derivatives of the Helmholtz residual energy of association can be calculated, in order to obtain the remainder of the thermodynamic properties. The implementation and use of this generalized procedure for the calculation of the fraction of nonbonded molecules within the soft-SAFT context is slightly more time-consuming than when the analytical expression is used. However, it is very rewarding in terms of calculation procedure to have a flexible algorithm that can be applied to a vast number of cases without having to derive the specific expressions for each case. The results of using this approach together with the above-mentioned association scheme to model the vapor–liquid equilibria of mixtures of poly(ethylene glycol) and different alkanols are presented in Figures 5 and 6. The alkanols studied were methanol and ethanol from Kim et al.³⁴ and 2-propanol from Zafarani-Moattar and Yeganeh.³⁵ The molecular weights of the polymers were 600 g/mol for the mixtures of ethanol and methanol and 200, 300, and 1000 g/mol for the 2-propanol mixture. Figure 5 shows the results obtained with the soft-SAFT EoS at 303.15 K. A larger correction of the mixture is needed for the methanol ($\xi = 1.140$) than for ethanol ($\xi = 1.040$). Although the binary parameter is not directly connected to the association term, the smaller size of the methanol molecule can give a greater emphasis on the association contribution to the phase equilibria behavior. The global behavior is then corrected with the binary interaction parameter. The solubility of 2-propanol in poly(ethylene glycol) of three different molecular weights, 200, 300, and 1000 g/mol, at 298.15 K, is presented

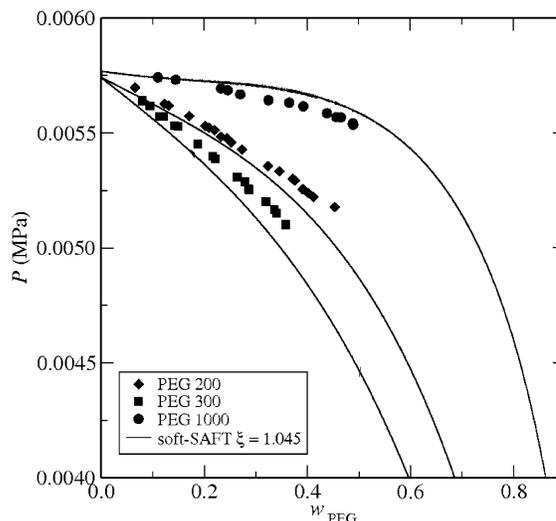


Figure 6. Vapor–liquid equilibria of the mixture poly(ethylene glycol)/2-propanol at 298.15 K modeled with the soft-SAFT EoS. The experimental data is from Zafarani-Moattar and Yeganeh.³⁵

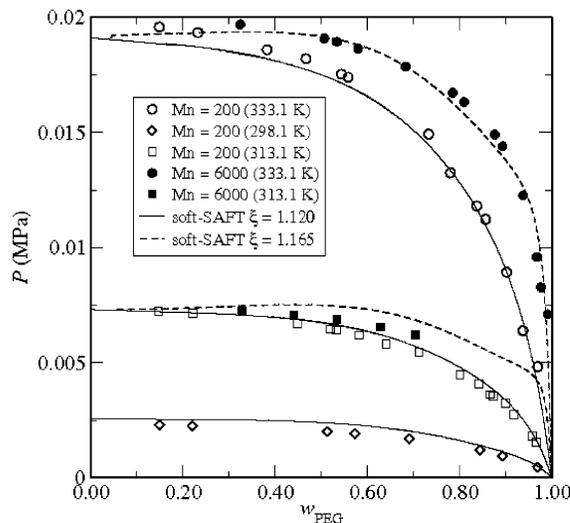


Figure 7. Modeling of the vapor–liquid equilibria of the mixture poly(ethylene glycol)/water with the soft-SAFT EoS. The molecular weight of the polymers modeled is 200 and 6000 g/mol. Experimental data from Herskowitz and Gottlieb.³⁶

in Figure 6. The soft-SAFT is able to capture the change of the vapor–liquid behavior with molecular weight of the polymer. In this case, only one small binary interaction parameter ($\xi = 1.045$) is required to accurately model all polymer molecular weights, which is very similar to the one used for ethanol.

Figure 7 shows the description of the vapor–liquid equilibria for the system poly(ethylene glycol)/water³⁶ for two polymer molecular weights, 200 and 6000 g/mol, in a temperature range between 298.1 and 333.1 K. Like alkanols, water has the ability to form hydrogen bonds with the polymer's hydroxyl groups in the chain ends or with other water molecules. Again, a single molecular-weight-dependent binary interaction parameter was required to model these mixtures: for PEG 200, a value of $\xi = 1.120$ was used, while for PEG 6000, $\xi = 1.165$ was considered. These values are similar to those used for methanol, and they are related to the magnitude of the energetic interaction that takes place between the polymer and the solvent. The soft-SAFT EoS description of the vapor–liquid equilibria of this system presents some abnormalities, especially for PEG 6000 at 313.1 K. This behavior is due to the strong energetic interactions between water and poly(ethylene glycol), which the inclusion

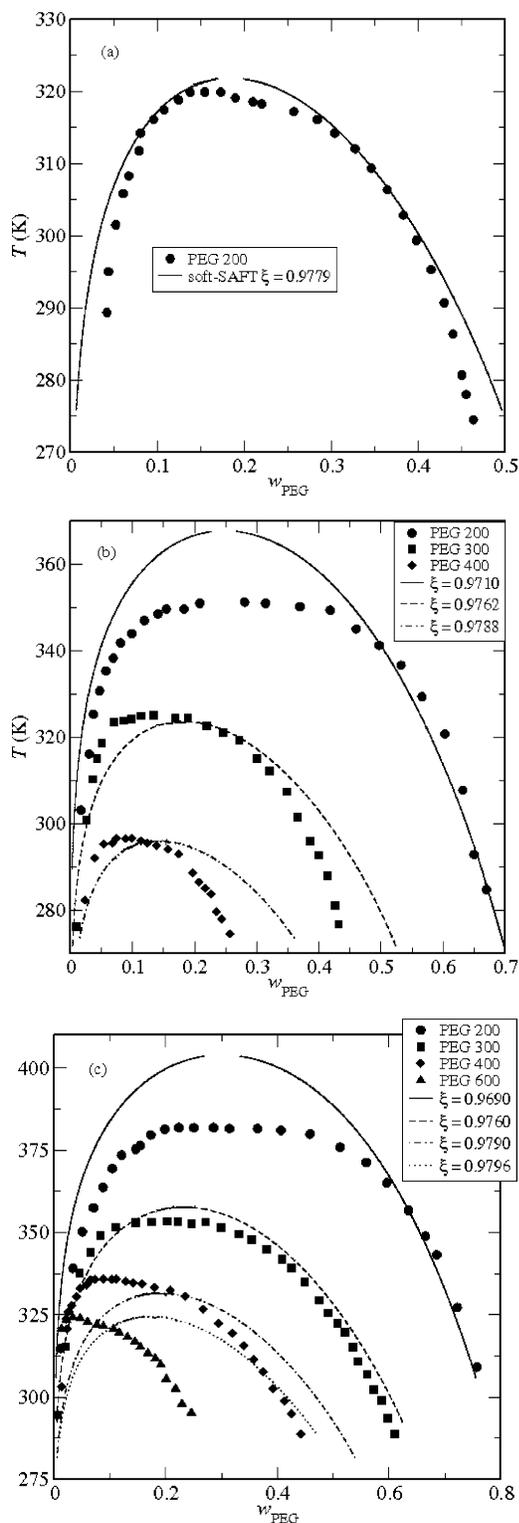


Figure 8. Description of the liquid–liquid equilibria of the mixtures (a) PEG/toluene, (b) PEG/ethylbenzene, and (c) PEG/*n*-propylbenzene with the soft-SAFT EoS. Experimental data is from Sabadini.⁴

of a molecular-weight-dependent binary interaction parameter is not able to describe.

Liquid–Liquid Equilibria. The experimental data of the mixture of poly(ethylene glycol) and toluene, ethylbenzene, and *n*-propylbenzene from Sabadini⁴ was modeled with the soft-SAFT EoS. These systems present a liquid–liquid phase diagram with UCST. The molecular weight of the polymer used ranged from 200 to 600 g/mol, and the pressure at which these systems were measured was 0.1 MPa. The polydispersity of

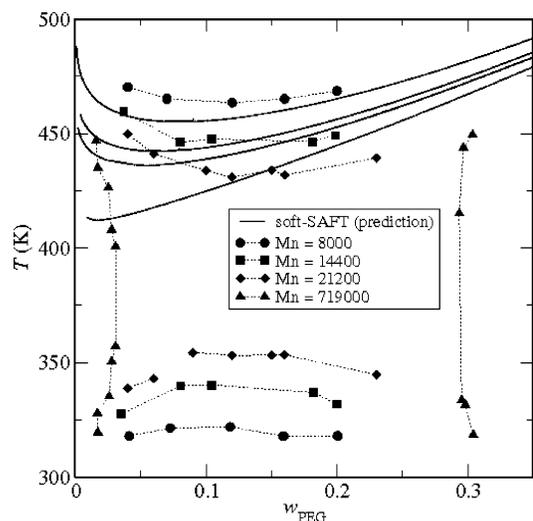


Figure 9. Prediction of liquid–liquid equilibria of the mixture poly(ethylene glycol)/*tert*-butyl acetate with the soft-SAFT EoS. Experimental data from Saeki et al.³⁷

these polymers ranged from 1.0 to 1.5, for which the polymers can be considered monodisperse. Figure 8a shows the model description of the PEG/toluene mixture for the PEG 200. The agreement with the experimental data is very good when a binary interaction parameter $\xi = 0.9779$ is used. The modeling of the system PEG/ethylbenzene is depicted in Figure 8b, where polymer molecular weights of 200, 300, and 400 g/mol were considered. Again, the model can describe the system behavior accurately when using a molecular-weight-dependent binary interaction parameter, which becomes closer to 1 with increasing molecular weight, as seen previously for other mixtures considered in this work, as for the PEG/propane system. The soft-SAFT description of the system PEG/*n*-propylbenzene is difficult to achieve, especially for the polymer with the highest molecular weight, as shown in Figure 8c. The molecular weight of the polymer used ranged from 200 to 600 g/mol. In the latter, even with the use of a binary interaction parameter, the model was not able to correctly describe the shift of the phase diagram with increasing molecular weight, overpredicting the composition of the mixture critical point. For these systems, a molecular-weight-dependent binary interaction parameter was necessary to achieve a reasonable description of the liquid–liquid-phase equilibria. This is more notorious for the PEG/*n*-propylbenzene, where the range of molecular weights is larger. With the existence of this dependency, the equation can achieve a good description of the critical temperature, but it is not able to follow the trend of the critical composition. A characteristic worthy of this system is also the sensitivity of the soft-SAFT phase equilibria description to the binary interaction parameters. For the system PEG/*n*-propylbenzene, this parameter ranges from 0.9690 to 0.9796, which is only a 1% change.

Finally, Figure 9 shows the soft-SAFT description of the liquid–liquid-phase equilibria of the mixture poly(ethylene glycol)/*tert*-butyl acetate at 0.1 MPa. The experimental data of Saeki et al.³⁷ indicates that the liquid–liquid equilibria phase diagram for this system presents both a LCST and a UCST for low polymer molecular weights (8000, 14 400, and 21 200 g/mol) and changes to an hourglass-shape phase diagram for the highest polymer molecular weight considered (719 000). No association was considered to exist between the solvent (*tert*-butyl acetate) and the polymer. As shown in Figure 9, the soft-SAFT EoS can predict reasonably well the LCST of the *tert*-butyl acetate with poly(ethylene glycol) 8000–21 200 g/mol

mixtures and its change with molecular weight. One of the shortcomings of the soft-SAFT model is here apparent. Because of a limitation of the temperature and density range of the Lennard-Jones reference term derived from Johnson et al.⁴⁰ fitted to the simulation data, the soft-SAFT EoS, using this reference equation, is not able to model the UCST. This matter was already addressed for polystyrene (PS) mixtures.⁴¹ In the PS case, the Lennard-Jones reference fluid EoS of Kolafa and Nezbeda⁴² was used, instead of the one from Johnson et al.⁴⁰ However, in the present case, it also failed to predict the UCST. Regarding the PEG 719 000 g/mol mixtures, the model also fails to describe the hourglass shape.

Conclusions

The soft-SAFT EoS was used in this work to model the phase equilibria of poly(ethylene glycol) mixtures with different solvents. The main characteristic of this polymer is the existence of association sites, which, in this case, were considered to be the hydroxyl end groups, where polymer and/or solvent molecules can form hydrogen bonds. This behavior was modeled using the TPT1 term of Wertheim within the SAFT approach.

The solubility of gases such as nitrogen, carbon dioxide, and propane in poly(ethylene glycol) was successfully described by the soft-SAFT model, using a single binary interaction parameter in all cases. The vapor–liquid equilibria of the mixtures PEG/benzene, PEG/methanol, PEG/ethanol, and PEG/2-propanol were also described with the soft-SAFT EoS. A binary interaction parameter was used for all mixtures. It should be noticed that this parameter has a value that is <1 for non-hydrogen bonding solvents and a value slightly >1 when modeling the *n*-alkanols and water. This indicates that nonassociating molecules such as the studied gaseous or aromatic compounds have a different impact on the phase equilibria description by the soft-EoS compared to associating liquid compounds such as water and *n*-alkanols at the conditions studied.

The liquid–liquid phase equilibria description of the mixtures poly(ethylene glycol)/toluene, poly(ethylene glycol)/ethylbenzene, and poly(ethylene glycol)/*n*-butylbenzene by the soft-SAFT EoS was successfully accomplished using a binary interaction parameter close to unity. The EoS is very sensitive to the value of the binary interaction parameter, especially when calculating UCST phase diagrams. They also depend on the molecular weight of the polymer.

The modeling of the liquid–liquid equilibria of the mixture poly(ethylene glycol)/*tert*-butyl acetate was accomplished for the LCST of the phase diagram. Limitations of the reference equation of state used in soft-SAFT prevented the correct modeling of the UCST of this mixture.

Acknowledgment

Partial financial support for this work has been provided by the Portuguese government (Project POCTI/43356/2001), the Spanish government (Project CTQ2005-00296/PPQ), and the Catalan government (Project 2005SGR-00288). N.P. acknowledges the Ph.D. scholarship (Grant SFRH/BD/11041/2002) from “Fundação para a Ciência e Tecnologia”.

Supporting Information Available: Figures depicting a description of the soft-SAFT EoS of the VLE of PEG/CO₂ mixtures, model description (using soft-SAFT) of a PEG 1500/propane mixture at various temperatures, and description of the VLE (using soft-SAFT) of a PEG 4000/propane mixture. This

material is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- (1) Parveen, S.; Sahoo, S. K. Nanomedicine—Clinical applications of polyethylene glycol conjugated proteins and drugs. *Clin. Pharmacokinet.* **2006**, *45*, 965–988.
- (2) Osada, K.; Kataoka, K. Drug and gene delivery based on supramolecular assembly of PEG–polypeptide hybrid block copolymers. *Adv. Polym. Sci.* **2006**, *202*, 113–153.
- (3) Annunziata, O.; Asherie, N.; Lomakin, A.; Pande, J.; Ogun, O.; Benedek, G. B. Effect of polyethylene glycol on the liquid–liquid phase transition in aqueous protein solutions. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 14165–14170.
- (4) Sabadini, E. *Estudo Físico-químico de polietileno glicol com água e solventes aromáticos*; Universidade Estadual de Campinas: Campinas SP, Brazil, 1993.
- (5) Chapman, W. G.; Gubbins, K. E.; Jackson, G.; Radosz, M. New Reference Equation of State for Associating Fluids. *Fluid Phase Equilib.* **1989**, *52*, 31–38.
- (6) Wertheim, M. S. Fluids With Highly Directional Attractive Forces. 1. Statistical Thermodynamics. *J. Stat. Phys.* **1984**, *35*, 19–34.
- (7) Wertheim, M. S. Fluids With Highly Directional Attractive Forces. 2. Thermodynamic Perturbation-Theory and Integral-Equations. *J. Stat. Phys.* **1984**, *35*, 35–47.
- (8) Wertheim, M. S. Fluids With Highly Directional Attractive Forces. 3. Multiple Attraction Sites. *J. Stat. Phys.* **1986**, *42*, 459–476.
- (9) Wertheim, M. S. Fluids With Highly Directional Attractive Forces. 4. Equilibrium Polymerization. *J. Stat. Phys.* **1986**, *42*, 477–492.
- (10) Blas, F. J.; Vega, L. F. Thermodynamic behaviour of homonuclear and heteronuclear Lennard-Jones chains with association sites from simulation and theory. *Mol. Phys.* **1997**, *92*, 135–150.
- (11) Blas, F. J.; Vega, L. F. Prediction of binary and ternary diagrams using the statistical associating fluid theory (SAFT) equation of state. *Ind. Eng. Chem. Res.* **1998**, *37*, 660–674.
- (12) Gil-Villegas, A.; Galindo, A.; Whitehead, P. J.; Mills, S. J.; Jackson, G.; Burgess, A. N. Statistical associating fluid theory for chain molecules with attractive potentials of variable range. *J. Chem. Phys.* **1997**, *106*, 4168–4186.
- (13) Gross, J.; Sadowski, G. Perturbed-Chain SAFT: An equation of state based on a perturbation theory for chain molecules. *Ind. Eng. Chem. Res.* **2001**, *40*, 1244–1260.
- (14) Gross, J.; Sadowski, G. Modeling polymer systems using the perturbed-chain statistical associating fluid theory equation of state. *Ind. Eng. Chem. Res.* **2002**, *41*, 1084–1093.
- (15) Chen, C. K.; Duran, M. A.; Radosz, M. Phase Equilibria in Polymer Solutions. Block-Algebra, Simultaneous Flash Algorithm Coupled With SAFT Equation of State, Applied to Single-Stage Supercritical Antisolvent Fractionation of Polyethylene. *Ind. Eng. Chem. Res.* **1993**, *32*, 3123–3127.
- (16) Chen, S. J.; Economou, I. G.; Radosz, M. Phase-Behavior of LCST and UCST Solutions of Branchy Copolymers—Experiment and SAFT Modeling. *Fluid Phase Equilib.* **1993**, *83*, 391–398.
- (17) Kleiner, M.; Tumakaka, F.; Sadowski, G.; Latz, H.; Buback, M. Phase equilibria in polydisperse and associating copolymer solutions: Poly(ethene-co-(meth)acrylic acid)-monomer mixtures. *Fluid Phase Equilib.* **2006**, *241*, 113–123.
- (18) Kouskoumvekaki, I.; Krooshof, G.; Michelsen, M.; Kontogeorgis, G. Application of the Simplified PC-SAFT Equation of State to the Vapor–Liquid Equilibria of Binary and Ternary Mixtures of Polyamide 6 with Several Solvents. *Ind. Eng. Chem. Res.* **2004**, *43*, 826–834.
- (19) Wiesmet, V.; Weidner, E.; Behme, S.; Sadowski, G.; Arlt, W. Measurement and modelling of high-pressure phase equilibria in the systems polyethylene glycol (PEG)–propane, PEG–nitrogen and PEG–carbon dioxide. *J. Supercrit. Fluids* **2000**, *17*, 1–16.
- (20) Pedrosa, N.; Pamies, J. C.; Coutinho, J. A. P.; Marrucho, I. M.; Vega, L. F. Phase Equilibria of Ethylene Glycol Oligomers and Their Mixtures. *Ind. Eng. Chem. Res.* **2005**, *44*, 7027–7037.
- (21) Scott, R. L.; van Konynenburg, P. H. Static properties of solutions. Van der Waals and related models for hydrocarbon mixtures. *Discuss. Faraday Soc.* **1970**, *49*, 87–97.
- (22) Gubbins, K. E.; Two, C. H. Thermodynamics of polyatomic fluid mixtures. I. Theory. *Chem. Eng. Sci.* **1978**, *33*, 863–868.
- (23) Dias, A. M. A.; Pamies, J. C.; Coutinho, J. A. P.; Marrucho, I.; Vega, L. F. SAFT modeling of the solubility of gases in perfluoroalkanes. *J. Phys. Chem. B* **2004**, *108*, 1450–1457.
- (24) Llovel, F.; Pamies, J. C.; Vega, L. F. Thermodynamic properties of Lennard-Jones chain molecules: Renormalization-group corrections to

a modified statistical associating fluid theory. *J. Chem. Phys.* **2004**, *121*, 10715–10724.

(25) Pamies, J. C.; Vega, L. F. Vapor–liquid equilibria and critical behavior of heavy *n*-alkanes using transferable parameters from the soft-SAFT equation of state. *Ind. Eng. Chem. Res.* **2001**, *40*, 2532–2543.

(26) Pamies, J. C.; Vega, L. F. Critical properties of homopolymer fluids studied by a Lennard-Jones statistical associating fluid theory. *Mol. Phys.* **2002**, *100*, 2519–2529.

(27) Pedrosa, N.; Vega, L. F.; Coutinho, J. A. P.; Marrucho, I. M. Phase Equilibria Calculations of Polyethylene Solutions from SAFT-Type Equations of State. *Macromolecules* **2006**, *39*, 4240–4246.

(28) Dias, A. M. A.; Carrier, H.; Daridon, J. L.; Pamiès, J. C.; Vega, L. F.; Coutinho, J. A. P.; Marrucho, I. M. Vapor–liquid equilibrium of carbon dioxide–Perfluoroalkane mixtures: Experimental data and SAFT modeling. *Ind. Eng. Chem. Res.* **2006**, *45*, 2341–2350.

(29) Kouskoumvekaki, I.; von Solms, N.; Lindvig, T.; Michelsen, M.; Kontogeorgis, G. Novel Method for Estimating Pure-Component Parameters for Polymers: Application to the PC-SAFT Equation of State. *Ind. Eng. Chem. Res.* **2004**, *43*, 2830–2838.

(30) Crupi, V.; Jannelli, M. P.; Magazu, S.; Maisano, G.; Majolino, D.; Migliardo, P.; Sirna, D. Rayleigh wing and Fourier transform infrared studies of intermolecular and intramolecular hydrogen bonds in liquid ethylene glycol. *Mol. Phys.* **1995**, *84*, 654–652.

(31) Economou, I. G. Statistical associating fluid theory: A successful model for the calculation of thermodynamic and phase equilibrium properties of complex fluid mixtures. *Ind. Eng. Chem. Res.* **2002**, *41*, 953–962.

(32) Müller, E. A.; Gubbins, K. E. Molecular-based equations of state for associating fluids: A review of SAFT and related approaches. *Ind. Eng. Chem. Res.* **2001**, *40*, 2193–2211.

(33) Daneshvar, M.; Kim, S.; Culari, E. High-Pressure Phase Equilibria of Poly(ethylene glycol)–Carbon Dioxide Systems. *J. Phys. Chem.* **1990**, *94*, 2124–2128.

(34) Kim, J.; Choi, E.; Yoo, K.; Lee, C. S. Measurement of activities of solvents in binary polymer solutions. *Fluid Phase Equilib.* **1999**, *161*, 283–293.

(35) Zafarani-Moattar, M. T.; Yeganeh, N. Isopiestic Determination of 2-Propanol Activity in 2-Propanol + Poly(ethylene glycol) Solutions at 25 °C. *J. Chem. Eng. Data* **2002**, *47*, 72–75.

(36) Herskowitz, M.; Gottlieb, M. Vapor–Liquid Equilibrium in Aqueous Solutions of Various Glycols and Poly(ethylene glycols). 3. Poly(ethylene glycols). *J. Chem. Eng. Data* **1985**, *30*, 233–234.

(37) Saeki, S.; Kuwahara, N.; Nakata, M.; Kaneko, M. Upper and lower critical solution temperatures in poly(ethylene glycol) solutions. *Polymer* **1976**, *17*, 685–689.

(38) Booth, C.; Devoy, C. J. Thermodynamics of mixtures of poly(ethylene oxide) and benzene. *Polymer* **1971**, *12*, 309–319.

(39) Tan, S. P.; Adidharma, H.; Radosz, M. Generalized Procedure for Estimating the Fractions of Nonbonded Associating Molecules and Their Derivatives in Thermodynamic Perturbation Theory. *Ind. Eng. Chem. Res.* **2004**, *43*, 203–208.

(40) Johnson, J. K.; Zollweg, J. A.; Gubbins, K. E. The Lennard Jones Equation of State Revisited. *Mol. Phys.* **1993**, *78*, 591–618.

(41) Pedrosa, N.; Vega, L. F.; Coutinho, J. A. P.; Marrucho, I. M. Phase behavior of polystyrene systems as described by molecular-based equations of state. *Ind. Eng. Chem. Res.* **2006**, in press.

(42) Kolafa, J.; Nezbeda, I. The Lennard-Jones fluid—An accurate analytic and theoretically-based equation of state. *Fluid Phase Equilib.* **1994**, *100*, 1–34.

(43) Pamies, J. C.; Vega, L. F. Vapor–liquid equilibria and critical behavior of heavy *n*-alkanes using transferable parameters from the soft-SAFT equation of state. *Ind. Eng. Chem. Res.* **2001**, *40*, 2532–2543.

(44) Pamiès, J. C. Bulk and Interfacial Properties of Chain Fluids. Ph.D. Thesis, Universitat Rovira i Virgili, Tarragona, Spain, 2003.

(45) Design Institute for Physical Property Data Evaluated Standard Thermophysical Property Values, DIPPR 801, 1998.

(46) Blas, F. J. Aplicación de las técnicas de modelización molecular al cálculo del equilibrio de fases de sistemas multicomponentes y caracterización de materiales adsorbentes. Ph.D. Thesis, Universitat Rovira i Virgili, Tarragona, Spain, 1999.

Received for review January 29, 2007

Revised manuscript received April 10, 2007

Accepted April 23, 2007

IE0701672