PC-SAFT equation: a predictive tool to determine experimental conditions for polymer blend demixing

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ABSTRACT

The perturbed-chain statistical associating fluid theory equation of state (PC-SAFT) was applied to predict the phase behavior of polymer solutions in order to determine the pressure – temperature region for the high molecular weight polymer blend separation by using n-alkanes at high pressure and high temperature. The polymer blends selected were physical blends of polyethylene (PE)/ polystyrene (PS) and polypropylene (PP) / PS. The miscibility and immiscibility region of each polymer in different alkanes (n-pentane, n-hexane and n-heptane) was studied and, from this analysis, the experimental conditions of the polymer blend demixing were predetermined. The results obtained were validated with experimental data indicating that the PC-SAFT equation is a good tool to predict experimental conditions for the processing windows of polymer blend separation.

INTRODUCTION

The thermodynamics of polymer solutions plays a fundamental role in polymerization and polymer processing problems. Solubility and phase separation data are needed to evaluate and design new processes [1, 2]. In general, the equilibrium information is obtained from experimental studies. However, this kind of data is difficult to obtain for polymer systems. The "physics" of polymer solutions is more complicated than that of low molecular weight fluid systems. Consequently, in order to reduce experimental effort and costs, good predictive equilibrium models are needed. The prediction of polymer-solvent phase behavior is very difficult due to the large difference in size between the polymers and the solvent molecules.

The high nonideality of these systems needs physically based EoS for an accurate phase behavior description [3, 4]. For this reason, the use of lattice models such as the Sanchez-Lacombe [5] or EoS models like the PC-SAFT [6] has been proposed [1, 7]. The Sanchez-Lacombe (S-L) EoS is derived from a lattice-fluid model that accounts for the compressibility of a solution, or the free volume, by introducing holes into the lattice [5]. The major benefits of the S-L EoS are that it is very easily implemented and it can be used to interpolate data. It is also possible to use the S-L EoS to calculate the phase behavior of binary polymer-supercritical fluid (SCF) solvent and ternary polymer-SCF solvent-co-solvent mixtures [2, 8-11]. However, the performance of this equation is only fair [1].

Chapman et al. derived the statistical associating fluid theory (SAFT) equation of state, by assuming molecules as chains of connected spherical segments [12]. Applying Wertheim's thermodynamic perturbation theory of first order (TPT1) [13-16] and extending it to mixtures, Huang and Radosz [17, 18] proposed a modification of the SAFT equation of state and determined pure-component parameters for several

substances, including polymers. Gross and Sadowski [6] have proposed the perturbed-chain SAFT (PC-SAFT) by applying the perturbation theory of Barker and Henderson [19] to a hard-chain reference fluid. The three pure-component parameters required for nonassociating molecules were determined for numerous substances. In 2002, the same authors [20] applied the PC-SAFT equation to model the phase behavior of binary and ternary systems containing polymers, solvents and gases and they compared the equations proposed with the SAFT version of Huang and Radosz. The pure-component parameters of six polymers were determined by simultaneously fitting pure-component liquid-density data and binary phase equilibrium data. The parameters obtained were shown to be suitable for different mixtures and can thus be regarded as characteristic for polymers. The PC-SAFT equations were applied to binary mixtures of polymer and solvent, giving good results for vapor-liquid demixing as well as for high-pressure liquid-liquid equilibria at high temperatures (Lower Critical Solution Temperature, LCST) and low temperatures (Upper Critical Solution Temperature, UCST). Ternary mixtures of polymer-solvent and carbon dioxide were also investigated. The shift of vapor-liquid and liquid-liquid equilibria (LCST) toward higher pressures upon adding carbon dioxide was modeled. The three-phase vapor-liquid-liquid equilibrium was modeled with the PC-SAFT equations of state yielding good results. Arce et al. [21] compared the performance of the S-L and PC-SAFT EoS for the prediction of the cloud point in the system PP-n-pentane. These authors, using a single temperature dependent k_{ij} in both EoS, found that the PC-SAFT more accurately fitted the experimental data.

One important application of polymer-solvent equilibrium is the polymer blend demixing, where it is necessary to know the miscible and immiscible region of each polymer of the blend with the solvent selected for the separation. Physical blends,

particularly when involving polyolefins, are a versatile method for obtaining material with tailor-made properties. Usually, there are synergetic combinations of resin-resin properties. These kinds of materials are massively used in applications like automotive industry, where the blends rapidly replace engineering materials [22-24].

For a proper blend characterization it is fundamental to know its composition and morphology, the amount of compatibilizer used and its location in the blend. The separation of a polymer blend by traditional techniques, such as Soxhlet, is very difficult because of the high molecular weight of the polymer blend components. The use of a selective high temperature-high pressure near critical solvent is an interesting alternative to obtain a complete and fast separation. In previous works [25-27] a polymer blend separation method using high pressure-high temperature n-pentane and n-heptane was proposed. The polymer blends demixed were PE/PS and PP/PS physical blends. The separation was achieved through the solubilization of the polyolefin phase. The solubilization of PP and/or PE can be reached by selecting suitable experimental conditions. The selection of these conditions for each polymer can be made using an EoS.

In this work, the perturbed-chain statistical associating fluid theory (PC-SAFT) equation of state was applied to predict the phase behavior of polymer solutions in order to determine the high molecular weight polymer blend separation region using high pressure-high temperature n-alkanes. The polymer blends under study were the physical blends PE/PS and PP/PS. The miscibility and immiscibility regions of each polymer in different alkanes (n-pentane, n-hexane and n-heptane) were studied to determine the processing window for the polymer blend demixing.

The PC-SAFT

The PC-SAFT is a modification of the SAFT equation developed by applying the perturbation theory of Barker and Henderson [19] to a hard-chain reference fluid. This equation of state is applicable to mixtures of small spherical molecules such as gases, non-spherical solvents, and chain-like polymers. In the framework of PC-SAFT, molecules are assumed to be chains of freely joined spherical segments exhibiting attractive forces amongst each other. The model is based on perturbation theories. The basic idea of a perturbation theory is to divide the interactions of molecules into a repulsive part and a contribution due to the attractive part of the potential. The repulsive interactions of the PC-SAFT equation of state are described with a hard-chain expression derived by Chapman et al. [28]. The attractive interactions are further separated into dispersive interactions and a contribution due to association. The compressibility factor is then calculated as the sum of the ideal gas contribution ($Z^{id} = 1$), the hard-chain term (hc), the dispersive part (disp, chain), and the contribution due to association (assoc) as follows:

$$Z = 1 + Z^{hc} + Z^{disp,chain} + Z^{assoc} \tag{1}$$

where Z is the compressibility factor with $Z=Pv/RT$, P is the pressure, v is the molar volume, and R denotes the gas constant.

A new dispersion term was developed for the PC-SAFT equation of state, which explicitly accounts for the chain-length dependences of the interactions. The dispersion term was obtained by extending the perturbation theory of Barker and Henderson [19] to chain molecules. The chain-length dependence of the dispersive interactions is thereby based on a molecular theory derived by Liu and Hu [29]. This theory takes into account that a segment within a chain is bonded to neighbor segments. It also considers the effect of next-to-nearest-neighbor segments on the interactions of a segment. The same as for the original and other SAFT-type equations

of state, sets of three pure component parameters are required for nonassociating molecules, namely, the segment diameter σ_i (length unit: Å), the number of segments of type i in a chain (m_i), and the segment dispersion energy ε_i/k (temperature unit: K). Additionally, a binary interaction parameter (k_{ij}) is required to model the system. More detailed information about the equation of state can be found in its author's original publication [6].

RESULTS AND DISCUSSION

The equation PC-SAFT was applied to the systems PE/PS and PP/PS, considering the solvents n-pentane, n-hexane and n-heptane. For these components the pure component parameters reported by Gross and Sadowski were used [6, 20] for the phase behavior predictions. In the case of linear low density polyethylene (LLDPE) the parameters used were selected supposing that the PVT behavior is similar to LDPE, due to their chemical architecture are similar. These parameters were tuned to experimental data [30]. Analogous supposition was made by other authors for modeling with S-L Eos [31]. The component properties and parameters used are summarized in Tables 1 and 2. Phase equilibrium calculations were done with the software GPEC [32, 33]. Even though the methods for constructing Global Phase Equilibrium Diagrams (GPED) [34] cannot yet be generally applied to polymer systems, all the Pxy diagrams shown in this work were successfully generated using a different option available in GPEC [33]. For the calculation of a Pxy or Txy diagram the continuation method [35] was used, starting from a user-provided initial point instead of intersected points at the GPED. The polymers were assumed to be monodisperse, with a molecular weight equal to the $\overline{M_w}$ (weight-average molecular weight). Taking into account the high polidispersity index of the polymers in Table I,

the use of $\overline{M_w}$ or the number average molecular weight ($\overline{M_n}$) could generate different predictions. However, the differences are not so significant due to the high molecular weight of the polymers under study.

The methodology used for the studies includes an initial analysis of temperature effect considering a zero value for the interaction parameter ($k_{ij}=0$), followed by a k_{ij} variation study at constant temperature. Please note that the temperature selected was 453 K because at this temperature both, PE and PP are entirely melted (see Table I). It is known that semicristalline polymers dissolve at temperatures above their melting temperature, or in some cases, at slightly lower temperatures [36]. On the other hand, this temperature is 76 K higher than the PS glass transition temperature (Tg), and it is a typical processing temperature for this amorphous resin because at this temperature the polymer matrix is softened enough to give an adequate processing viscosity. Consequently, this temperature was selected for all systems studied.

PE-n-alkanes Systems

The results of phase separation pressure as a function of blend composition for PE-n-pentane, with $k_{ij} = 0$ at different temperatures, are shown in Fig. 1. The region above the curve corresponds to total miscibility conditions, where only one phase is present. The zone under the curve is a two phase region composed of two liquid phases. The pressure to reach the total miscibility increases as the temperature increases. This is a typical LCST behavior in agreement with previous experimental works for the same kind of system but of lower molecular weight [2, 32, 37- 40].

The influence of the interaction parameter on the phase behavior at constant temperature is shown in Fig. 2, for T= 453 K. It can be observed that the phase separation pressure increases as the k_{ij} value increases. The maximum pressure

necessary to reach the entire miscibility is around 300 bar when $k_{ij} = 0.02$. Experimental data of PE with different molecular weight and polydispersity from [30] were used to estimate the more adequate value for the interaction parameter. In all cases, the PE polymers were modeled as monodisperse. The fitting results are shown in Fig. 3. The k_{ij} value for the PC-SAFT equation that better reproduces the experimental data varies with the polymer molecular weight, as shown in Table 3. The higher the molecular weight, the higher the k_{ij}. These results are in agreement with the fitting performed when using the Sanchez-Lacombe EoS with the same assumption [2]. Besides, from the values in Table 3, it can be concluded that the more appropiate interaction parameter values to represent the PE-n-pentane behavior are close to zero, according to the characteristics of PE used in this work.

The effect of solvent molecular weight was analyzed by comparing the above results with phase equilibrium predictions of PE-n-hexane systems. The methodology is similar to that used in the PE-n-pentane mixtures. Initially, a study of the phase equilibrium at different temperatures for $k_{ij} = 0$, and later, for constant temperature (453K) and variating $k_{ij,}$ was performed. The results obtained are shown in Figs. 4 and 5, respectively. It was observed that at higher temperatures, higher pressures are necessary to reach the homogeneity conditions (LCST behavior). Increments in k_{ij} produce increments in separation pressure, similar to those seen in PE-n-pentane systems. The solvent size effect results in a decrease in the phase separation pressure, as can be observed in Figs. 1 and 2 (PE-n-pentane) and 4 and 5 (PE-n-hexane). For the PE-n-pentane system at 453 K and $k_{ij} =0$, the maximum pressure is about 129 bar, whereas for PE-n-hexane system, and for the same temperature and k_{ij} value, the maximum pressure is 40 bar.

PP-n-alkanes Systems

The results of the separation pressure for the system PP-n-pentane with the PP weight fraction at different temperatures and $k_{ij}=0$, are shown in Fig. 6. At higher temperatures, higher pressures are necessary to reach the miscibility zone, in agreement with LCST behavior observed by other researchers for this kind of system [8, 41-43]. Furthermore, the k_{ij} effect on equilibrium conditions was analyzed. Fig. 7 shows the results of phase separation pressure as a function of PP blend content (wt%), obtained at 453 K and for different k_{ij}. The separation pressure increases as this interaction parameter increases. In order to select the appropriate k_{ij} value, previous works were analyzed. Gross and Sadowski [20] achieved a good fit of experimental data of PP-n-pentane systems with a k_{ij} value of 0.0137, working with a polydispersed PP of 50400 g/mol (PD= 2.2), assumed it as monodisperse.

Taking into account that for PE-n-alkanes systems k_{ij} increases with the PE molecular weight, and considering the similar chemical nature of PP and PE molecules and the results obtained by Gross and Sadowski, the k_{ij} value for the system under study can be inferred. The appropriate value of k_{ij} could be higher than 0.0137 because the $\overline{M_w}$ of PP in the present work is about seven times higher than in [20]. For this reason, a curve calculated for $k_{ij} = 0.02$ was included in Figure 7. In this case the maximum pressure to get the homogeneous phase is of 72.3 bar, about 40% greater than the value obtained with $k_{ij}= 0$.

PS – n-alkanes Systems

The effects of temperature at $k_{ij} = 0$, for the system PS-n-pentane are shown in Fig. 8. The separation pressure, as a function of the PS weight fraction, presents a LCST behavior increasing with temperature. The maximum in separation pressure is between 120 and 200 bar approximately.

In Fig. 9, the separation pressure vs the PS content at 453K is shown for different k_{ij} values. It can be observed that the necessary pressure to reach the miscibility increases considerably with small increments of k_{ij} values, resulting in total immiscibility zones above certain k_{ij} values. The immiscibility zone is wider as the k_{ij} increases. A zero interaction parameter is unlikely for this kind of system, where the polymer molecule and solvent are very different in size and chemical structure. In order to obtain an estimation of the k_{ij} value for these systems, the fitting of experimental data of Saraf y Kiran [44] was carried out. The value obtained for low molecular weight PS ($\overline{M_w} = 9000\ g/mol$) in n-pentane is 0.02. This k_{ij} predicts the maximum pressure value very well but does not accurately fit the data in all the range analyzed.

From the above discussion, PC-SAFT predictions were performed assuming $k_{ij} = 0.018$ for different temperatures in order to avoid total immiscibility zones, knowing that this behavior is highly probable. Fig. 10 shows the results obtained, where two zones can be distinguished depending on the PS weight fraction. A UCST behavior is observed for weight fractions lower than 0.35 because the separation pressure decreases as temperature increases. Similar behavior was observed experimentally by other authors [44, 45]. However, PC-SAFT, with the $k_{ij} = 0.018$, predicts a LCST behavior for weight fractions higher than 0.35. It is clear that changing the k_{ij} value, the behavior changes from LCST to UCST and that, as expected, the k_{ij} must be larger than that of polyolefin-n-alkanes systems to give an accurate prediction.

The solvent size effect was also analyzed. Calculations at 453 K for $k_{ij} = 0.02$ were performed for three solvents: n-pentane, n-hexane and n-heptane. Fig. 11 shows the behavior predicted for the $k_{ij} = 0.02$. In this system, the higher the solvent molecular weight, the higher the PS immiscibility. These results are opposite to the bibliographic experimental data [44, 45], where the solvent size increment, from n-butane to n-hexane, decreases the separation phase pressure. This difference can be explained as follows. The modeling of this kind of system, where the solvent and the polymer have very low chemical affinity, is more complex, and a small change in the interaction parameter produces important changes in the phase behavior. There probably is a different k_{ij} value to each PS-alkane system, a fact that has not been taken into account in these predictions. On the other hand, we are using a $k_{ij} = 0.02$, value that adequately reproduces the behavior of a PS of $\overline{M_w} = 9000 \, g/mol$, much lower than the molecular weight of the PS under study.

Experimental conditions selection. Processing windows determination

According to the phase equilibrium predicted by the PC-SAFT equation and density data [26], the experimental conditions needed to carry out the polymer blend separation can be selected. This requires finding a region (processing window) where the solvent is miscible with PP or PE and immiscible with PS. Thus, a PP/PS or PE/PS blend will be separated by selective dissolution of PP or PE, leaving the PS insoluble. This processing window should be located in the region of low polymer weight fraction, in pressure-composition phase diagrams. The reason is to avoid a high viscosity solution due to high polymer weight fraction, where the solvent dissolves in the polymer and not the polymer in the solvent, as desired.

From Figs. 6 and 7 it can be observed that the pressure needed to reach the PP-n-pentane miscibility region is about 50-60 bar, depending on the temperature and

considering the more probable values for the interaction parameter according to the bibliography. For the PE (Figs. 1, 2, 4 and 5) the homogeneous region is achieved at a pressure higher than 140 bar, if low interaction parameters are considered. In the case of PS, the miscibility is obtained at a pressure of about 500 bar or higher, with k_{ij}=0.02, value found for a PS with lower molecular weight. Taking into account the high molecular weight of the PS under study, it is probable that k_{ij} will be higher, and then the immiscibility could be total.

It is well known that the polymer solubility increases with solvent density [46]. In a previous work [26], the density variation with respect to pressure was analyzed for n-pentane and n-heptane at different temperatures. A significant increment of density with pressure was observed. To carry out the polymer blend separation experiment it is important to increase the solvent density and to work in a zone where the pressure variations do not produce important changes in it. This is possible, for example, by working at pressures higher than 200 bar.

The operating pressure selected for polymer blend separation was 300 bar since the requisites stated above are satisfied at this pressure. This lead to a homogeneous phase containing PE or PP and the solvent, separated from another phase, rich in PS, therefore achieving the desired separation. The use of 300 bar instead of the minimum pressure required for complete miscibility was to obtain a faster dissolution of the solvent in the polymer matrix. On the other hand, the temperature selected was higher than the melting point of each polyolefin because, as explained above, all polymers are in a softened state at the selected temperature.

Verification of Processing Window Prediction with experimental results

The experiments of polymer blend separations were carried out with the processing windows from the theoretical analysis presented above. Initially, the selectivity of two

solvents (n-pentane and n-heptane) on pure polymers (PE, PP and PS) was evaluated. The experiments were performed at the selected pressure (300 bar) and at different temperatures ranging from 393 K to 493 K [25-27]. It was demonstrated that the n-alkanes analyzed were good solvents for both, PE and PP and bad solvents for the PS. For a given extraction time, the amount of dissolved polyolefin increases as temperature increases. The entire PE and PP phases are solubilized at temperatures higher than the corresponding melting point (429 K for the PP and 399 K for the PE). On the other hand, the very low solubility of PS was evident. Only a 2 wt% of the PS mass was solubilized at the highest temperature studied (250 ºC) when the solvent used was n-heptane.

These experimental results confirm the theoretical predictions made with the PC-SAFT EoS. At the selected pressure, 300 bar, total PE and PP solubilization can be obtained without the solubilization of PS.

The predicted experimental temperatures to carry out the polymer blend separation were corroborated by the solvent selectivity analysis mentioned above. Temperatures of 140 ºC and 180 ºC were used in the PE/PS and PP/PS blend separations, respectively. The total polymer phase separation was achieved, especially when the polyolefin is the major component. For the separation time studied, the extraction yield decreased with the increment of PS content. However, total demixing is possible if the sample is subjected to the separation process for a longer period of time. It can be concluded that the separation rate is inversely related to PS content. That is, as the PS content increases, the separation rate decreases. These results corroborate the efficiency of the PC-SAFT prediction, and demonstrate that the separation can be achieved with the experimental conditions selected from the theoretical analysis.

Additional experiments of pure PP and PE solubilization were carried out at pressures near those predicted by PC-SAFT, and at temperatures higher than the PE melting point. For example, it was proven that it is possible to obtain a single phase of PE with n-pentane working at 150 bar, as the modeling analysis predicts [27].

However, in the blend separation the process was favored by using higher pressures (300 bar) at the same temperature due to the density effect mentioned above and the increase in solvent fugacity with pressure.

CONCLUSIONS

The PC-SAFT equation proved to be a useful tool to predict the solvent-high molecular weight polymer phase behavior. In this case, the equation was used to predict the behavior of PE, PP and PS with n-alkanes, in order to determine experimental conditions to carry out PE/PS and PP/PS blend separations using high pressure near critical solvents. The LCST behavior for solutions of PE-n-pentane and PP-n-pentane as well as the UCST behavior for PS-n-alkanes systems were assessed. These predictions together with the effect of pressure on solvent density permitted to determine the processing window required for the polymer blend separation. The experimental results demonstrated that the predictions were adequate and sharp polymer blend separation was achieved.

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TABLES

Table 1. Properties and pure component PC-SAFT parameters of the polymers

		Polyethylene (PE)	Polypropylene (PP)	Polystyrene (PS)
POLYMER PROPERTIES	$\overline{M}_w$ **(g/mol)**	53000	345500	272000
	$\overline{M}_n$ **(g/mol)**	18000	67800	127000
	Polidispersity	2.94	5.1	2.14
	Tm (K)	399	429	-
	Tg (ºC)	169.15	285.15	377.15
PC-SAFT PARAMETERS	m/M^* **[mol/g]**	0.0263	0.02305	0.019
	σ **[Å]**	4.0217	4.1	4.1071
	ε/κ **[K]**	247.5	217.0	267.0

* The segment number m depends on the molecular mass M of a polymer. It is determined from m/M) by multiplying with the molecular mass M.

Table 2. Properties and pure component PC-SAFT parameters of the solvents

			n-pentane	n-hexane	n-heptane
SOLVENT	**PROPERTIES**	**Critic Temp. (K)**	469.7	507.6	540.2
		Critic pressure (bar)	33.7	30.25	27.4
		Critic Vol. (lt/mol)	0.3656	0.4333	0.4999
PC-SAFT	**PARAMETERS**	m **[-]**	2.6896	3.0576	3.4831
		σ **[Å]**	3.7729	3.7983	3.8049
		ε/κ **[K]**	231.20	236.77	238.40

Table 3. Polymer properties [30] and k_{ij} value used in the PC-SAFT predictions

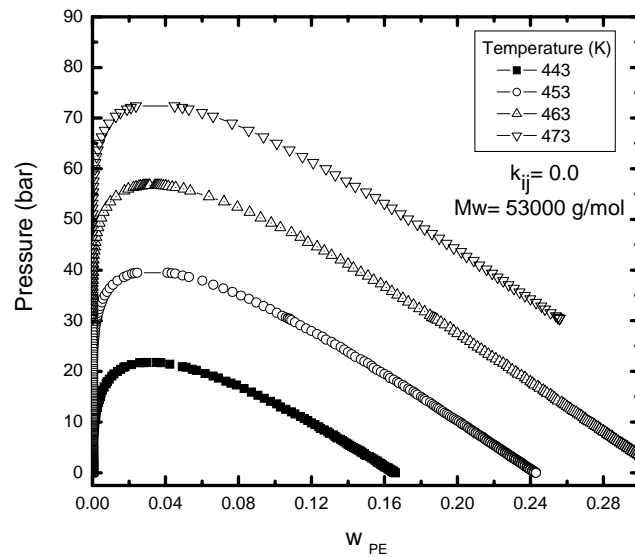| Name	$\overline{M}_w$ (g/mol)	PD	k_{ij}
PE 2.15	2150	1.14	-0.02
PE 16.4	16400	1.16	-0.006
PE 108	108000	1.32	0.0
PE 420	420000	2.66	0.0014

FIGURES

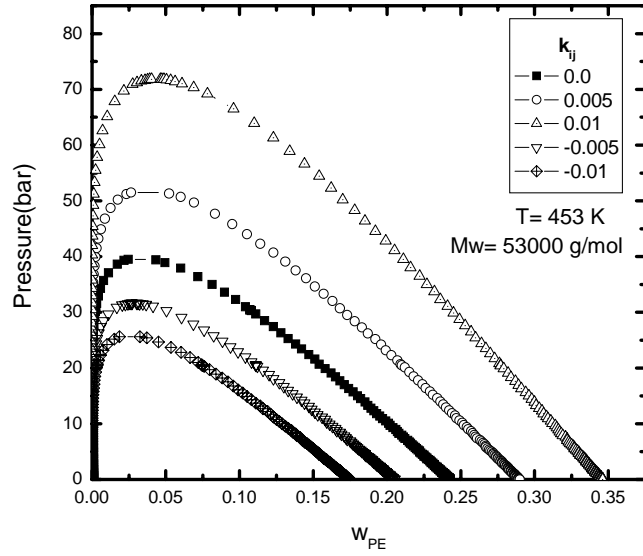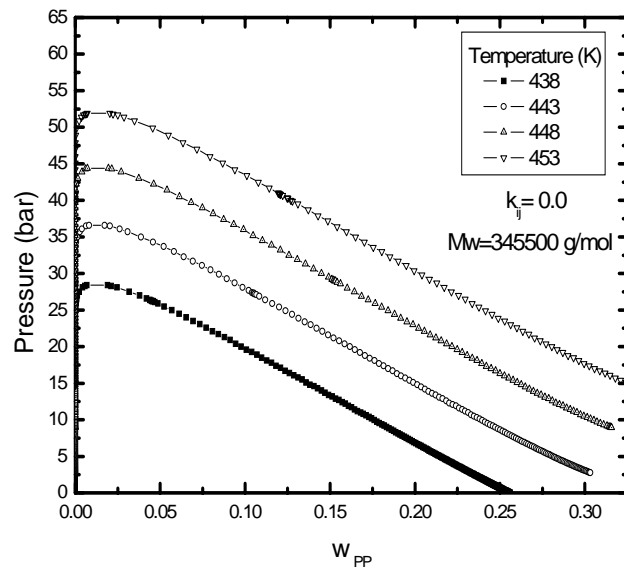**Fig. 1.** Variation of demixing pressure with polymer weight fraction for PE-n-pentane solutions at different temperatures (k_{ij} =0), calculated with PC-SAFT.

Fig. 2. Variation of demixing pressure with polymer weight fraction for PE-n-pentane solutions with different k_{ij} (T=453K), calculated with PC-SAFT.

Fig. 3. Variation of demixing pressure with polymer weight fraction and molecular weight, for PE-n-pentane solutions. Symbols are experimental points from [30]. Lines are the PC-SAFT predictions.

Fig. 4. Variation of demixing pressure with polymer weight fraction for PE-n-hexane solutions at different temperatures (k_{ij} =0), calculated with PC-SAFT.
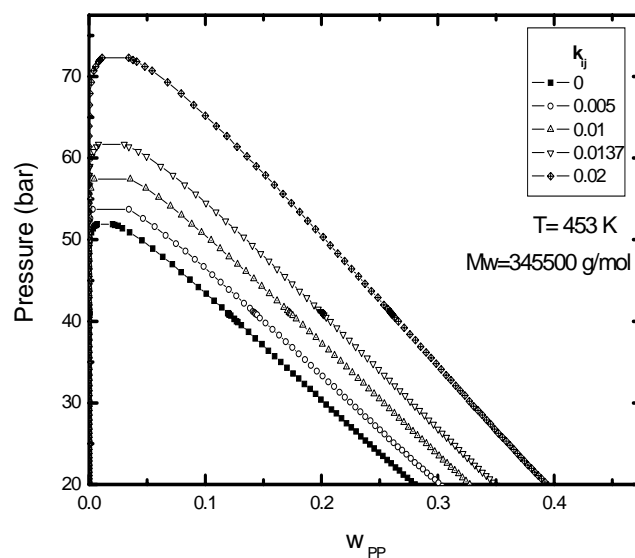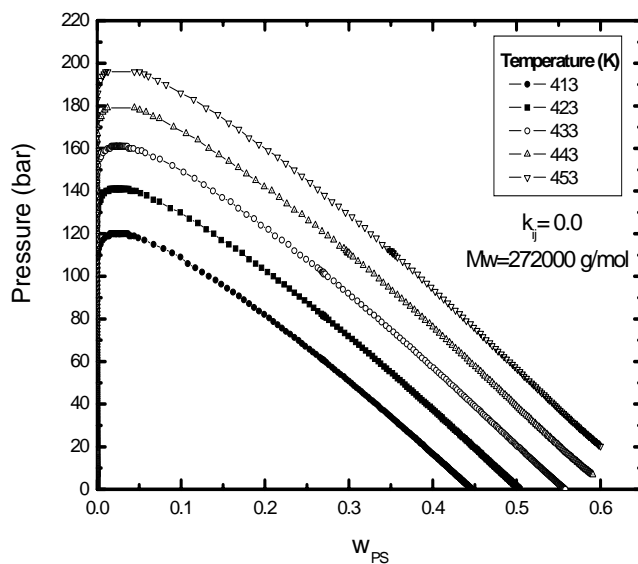
24

Fig. 5. Variation of demixing pressure with polymer weight fraction for PE-n-hexane solutions with different k_{ij} (T=453K), calculated with PC-SAFT.

Fig. 6. Variation of demixing pressure with polymer weight fraction for PP-n-pentane solutions at different temperatures (k_{ij} =0), calculated with PC-SAFT.
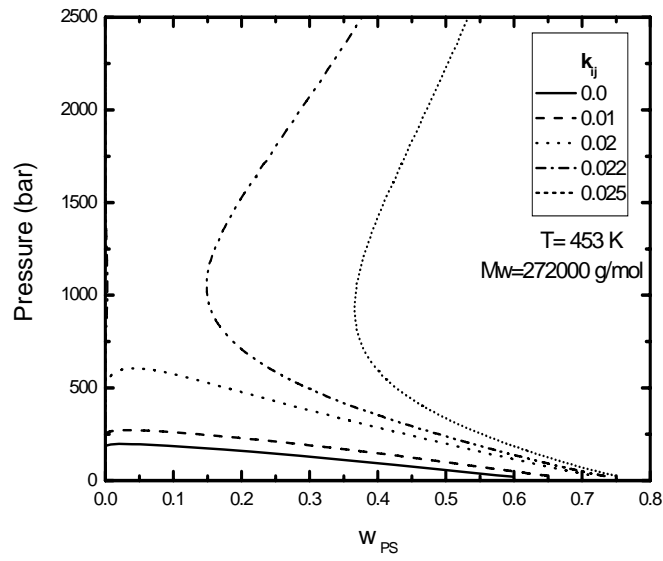
Fig. 7. Variation of demixing pressure with polymer weight fraction for PP-n-pentane solutions with different k_{ij} (T=453K), calculated with PC-SAFT.

Fig. 8. Variation of demixing pressure with polymer weight fraction for PS-n-pentane solutions at different temperatures (k_{ij} =0), calculated with PC-SAFT.

Fig. 9. Variation of demixing pressure with polymer weight fraction for PS-n-pentane solutions with different k_{ij} (T=453K), calculated with PC-SAFT.
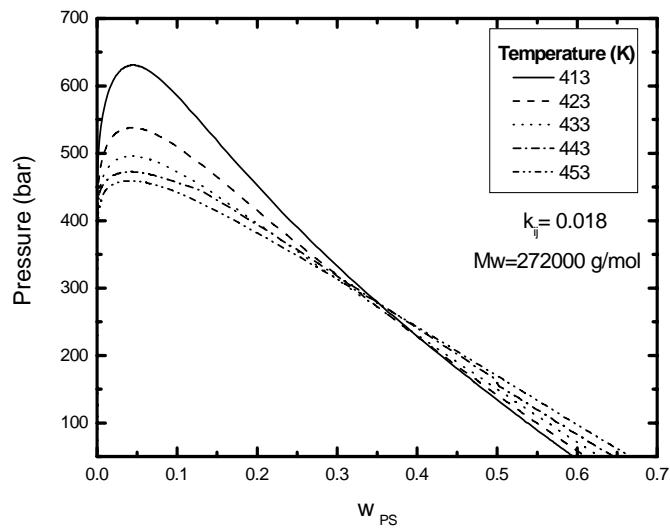

Fig. 10. Variation of demixing pressure with polymer weight fraction for PS-n-pentane solutions at different temperatures (k_{ij} =0.018), calculated with PC-SAFT.
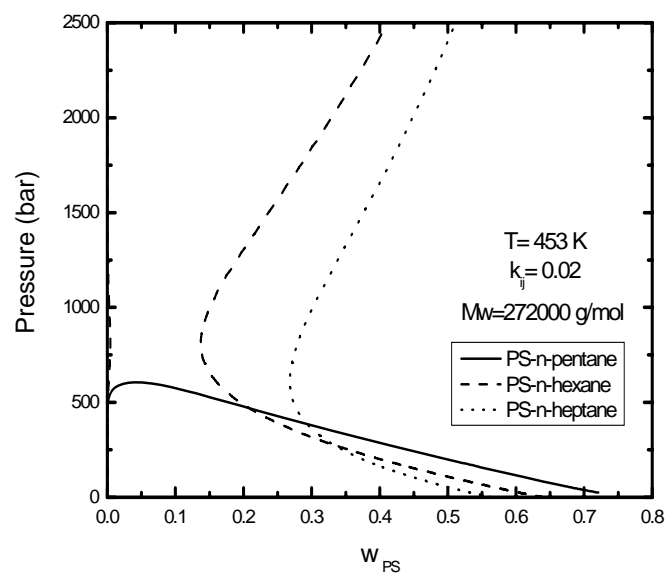
Fig. 11. Variation of demixing pressure with polymer weight fraction for PS-n-pentane, PS-n-hexane and PS-n-heptane solutions at 453 K and k_{ij} =0.02, calculated with PC-SAFT.

FIGURE CAPTIONS

Fig. 1. Variation of demixing pressure with polymer weight fraction for PE-n-pentane solutions at different temperatures (k_{ij} =0), calculated with PC-SAFT.

Fig. 2. Variation of demixing pressure with polymer weight fraction for PE-n-pentane solutions with different k_{ij} (T=453K), calculated with PC-SAFT.

Fig. 3. Variation of demixing pressure with polymer weight fraction and molecular weight, for PE-n-pentane solutions. Symbols are experimental points from [30]. Lines are the PC-SAFT predictions.

Fig. 4. Variation of demixing pressure with polymer weight fraction for PE-n-hexane solutions at different temperatures (k_{ij} =0), calculated with PC-SAFT.

Fig. 5. Variation of demixing pressure with polymer weight fraction for PE-n-hexane solutions with different k_{ij} (T=453K), calculated with PC-SAFT.

Fig. 6. Variation of demixing pressure with polymer weight fraction for PP-n-pentane solutions at different temperatures (k_{ij} =0), calculated with PC-SAFT.

Fig. 7. Variation of demixing pressure with polymer weight fraction for PP-n-pentane solutions with different k_{ij} (T=453K), calculated with PC-SAFT.

Fig. 8. Variation of demixing pressure with polymer weight fraction for PS-n-pentane solutions at different temperatures (k_{ij} =0), calculated with PC-SAFT.

Fig. 9. Variation of demixing pressure with polymer weight fraction for PS-n-pentane solutions with different k_{ij} (T=453K), calculated with PC-SAFT.

Fig. 10. Variation of demixing pressure with polymer weight fraction for PS-n-pentane solutions at different temperatures (k_{ij} =0.018), calculated with PC-SAFT.

Fig. 11. Variation of demixing pressure with polymer weight fraction for PS-n-pentane, PS-n-hexane and PS-n-heptane solutions at 453 K and k_{ij} =0.02, calculated with PC-SAFT.