Vapor–liquid equilibrium of copolymer + solvent mixtures: Thermodynamic modeling by two theoretical equations of state[☆]

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Abstract

Copolymers are increasing their importance from the commercial point of view, mainly due to their tuned physical properties for specific applications in the polymer manufacturing. Copolymers allow tailoring new materials with desirable features by blending specific copolymers, which contribute for the physical properties of the final material. The description of the fluid-phase equilibrium of copolymer + solvent mixtures by thermodynamic models is essential for the design of new manufacture processes. In this work, vapor–liquid equilibrium data for several copolymer + solvent mixtures were modeled using two theoretical equations of state: one based on the lattice gas theory (LGT) and another one based on the statistical association fluid theory, called perturbed chain-SAFT (PC-SAFT). The results show that the PC-SAFT equation of state provides a better representation of the experimental data in terms of pressure deviations.
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1. Introduction

Nowadays, most polymers are not polymer anymore, but are composed of different types of repeated monomer-units, forming the so-called copolymers. In Fig. 1 appears the representation of a copolymer with different monomer-units (types α and β) in the molecular chain.

Copolymers allow tailoring new materials with desirable physical properties by combining several different monomer-

units. The commercial interest for copolymers and their world-wide production have significantly increased in the last 20 years. However, vapor–liquid equilibrium (VLE) data for copolymer + solvent mixtures are still scarce [1]. Thus, it is important to describe the VLE of these mixtures by theoretical equations of state (EoS). There are a few studies in this direction. Gupta and Prausnitz [1] used the perturbed hard sphere chain (PHSC) EoS [2], with one or two binary parameters for each pair of different segments, to represent the VLE of 43 copolymer + solvent and homopolymer + solvent mixtures, but without presenting any deviations between experimental and calculated data. Lee and Danner [3] used a group-contribution lattice-fluid EoS [4,5] to represent the VLE for 16 copolymer + solvent solutions, also without any comment on deviations between experimental and calculated data. Silva et al. [6] used the Stryjek–Vera EoS [7], coupled with the Wong–Sandler mixing rule [8] and the UNIFAC group-contribution model for the activity coefficient [9] in order to describe the VLE of solutions of poly(styrene-*co*-butadiene) with pentane, toluene and cyclohexane, obtaining pressure deviations between 6.0 and 17.5%.

The lattice gas theories (LGT) introduced by Walker and Vause [10–12] and further studied by Goldstein and Walker [13] have been shown to be descriptive of a wide variety of

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Fig. 1. Molecular model for a copolymer of type poly(α-co-β), containing monomers α and β.

phase transition phenomena. In particular, methods have been developed for mapping experimental data on phase separations, as a function of various perturbations, into the global phase diagrams of the Hamiltonians studied. Detailed comparisons of the theory with experiments on the effect of electrolytes, dilute third components, pressure and isotopic substitution have shown that the models are sensitive to small variations in the intrinsic molecular properties which govern the existence of miscibility gap(s). The parametric trends in these studies are generally in accord with a specific, microscopic description of the important physics in the systems [14]. The use of lattice models is also well established in the polymer community. Taylor and Lipson [15] concluded that using an integral equation theory to study a lattice model of a polymer solution should be sufficient to capture many of the most important details of polymer phase transition. West et al. [16] used the single Sanchez–Lacombe lattice fluid equation of state to model both phases for a polymer-supercritical fluid-cosolvent system in a wide pressure range both volumetric and phase equilibrium properties for a cross-linked poly(dimethyl siloxane) phase in contact with CO_2 modified by a number of cosolvents. Liu and Cheng [17] used a simplified activity model for polymer solutions derived from the Gibbs–Helmholtz relation, in conjunction with the lattice theory to model polymer solutions. Vanderzande [18] made a complete study in his book about lattice models in polymer solutions.

In this work, two models are used to represent the VLE of 24 copolymer + solvent mixtures. One of the models is a LGT-based EoS, developed by Silva [19] and Mattedi et al. [20] and successfully applied to VLE calculations of polymer + solvent systems [21,22]. The other one is the PC-SAFT EoS, developed by Gross and Sadowski [23] and successfully extended to copolymers by Gross et al. [24] and Arce and Aznar [25]. The models are described below.

2. The LGT equation of state

A given fluid of volume V is represented by a lattice of coordination number Z_C (usually taken as 10.0) containing M cells of fixed volume V^*. Expressed as group-contributions, the LGT EoS is given by:

$$Z = \tilde{v}r \ln\left[\frac{\tilde{v}}{\tilde{v}-1}\right] + \frac{Z_C}{2}\tilde{v}r \ln\left[\frac{\tilde{v}-1+(q/r)}{\tilde{v}}\right] + l$$

$$-\frac{\tilde{v}\Psi(q/r)}{\tilde{v}-1+(q/r)}\sum_{i=1}^{n_c}\sum_{a=1}^{n_g}x_i v_i^a Q^a \frac{\Gamma^a-1}{\tilde{v}-1+(q/r)\Gamma^a} \quad (1)$$

where Z is the compressibility factor, v_i^a the number of groups of type a in a molecule of type i, Q^a the area parameter of group a and Ψ is an universal constant, taken as 1.0. The average number of segments occupied by a molecule in the lattice, r, the average number of close neighbors, q, and the reduced volume, $\tilde{v}$, are calculated by:

$$r_i = \sum_a v_i^a R^a \quad \text{and} \quad r = \sum_i x_i r_i \quad (2)$$

$$q = \sum_{i=1}^{n_c} x_i \sum_{a=1}^{n_g} v_i^a Q^a \quad (3)$$

$$\tilde{v} = \frac{V}{NrV^*} = \frac{v}{rv^*} \quad (4)$$

$$rV^* = \sum_{i=1}^{n_c} x_i \sum_{a=1}^{n_g} v_i^a V^a \quad (5)$$

$$rv^* = \sum_{i=1}^{n_c} x_i \sum_{a=1}^{n_g} v_i^a v^a \quad (6)$$

where R^a and V^a are the group-contribution parameters for the number of segments and hard-core volume, respectively, v^a the parameter for the molar hard-core volume for a group of type a and v^* is the cell molar volume, taken as $5.0\,cm^3$/mol. There are also others definitions:

$$\Gamma^a = \sum_{m=1}^{n_g} S^m \gamma^{ma} \quad (7)$$

$$S^m = \frac{\sum_{i=1}^{n_c} v_i^m x_i Q^m}{q} \quad (8)$$

$$\gamma^{ma} = \exp\left(-\frac{u^{ma}}{RT}\right) \quad (9)$$

where u^{ma} is the interaction energy between groups m and a. The fugacity coefficient for the model is:

$$\ln \hat{\phi}_i = -r_i \ln\left[\frac{\tilde{v}-1}{\tilde{v}-1+(q/r)}\right] + (1-l_i)\ln\left[\frac{\tilde{v}}{\tilde{v}-1+(q/r)}\right]$$

$$+ \frac{\Psi(q/r)(q_i-r_i)}{\tilde{v}-1+(q/r)} + \Psi\sum_{a=1}^{n_g} v_i^a Q^a \ln\left[\frac{\tilde{v}-1+(q/r)}{\tilde{v}-1+(q/r)\Gamma^a}\right]$$

$$- \frac{\Psi}{r}\sum_{k=1}^{n_c}\sum_{a=1}^{n_g} x_k v_k^a Q^a \frac{\sum_{e=1}^{n_g} v_i^e Q^e \gamma^{ea} - r_i}{\tilde{v}-1+(q/r)\Gamma^a} - \ln Z \quad (10)$$

As suggested by Chen and Kreglewski [26], v^a and u^{ma} are represented by:

$$v^a = v_\infty^a \cdot \left[1 - A^a \exp\left(\frac{-3u_0^{aa}}{RT}\right)\right]^3 \tag{11}$$

$$\frac{u^{ma}}{R} = \frac{u_0^{ma}}{R}\left(1 + \frac{B^{ma}}{T}\right) \tag{12}$$

Thus, the LGT EoS has five parameters for each group (v_∞^a, Q^a, u_0^{aa}/R, A^a and B^{aa}) and two parameters for interactions between different groups (u_0^{ma}/R and B^{ma}). Since the influence of the temperature on the hard-core volume for several solvent or monomer groups is quite low, the parameter A^a was fixed as equal to zero.

The copolymers were considered as mono-dispersed and not present in the vapor phase. For those copolymers whose molecular weight was not available, it was considered as equal to 100,000 g/mol, as suggested by Gupta and Prausnitz [1]. The solvents were considered as groups and their parameters were extracted from Lyrio et al. [22]. For those solvents whose parameters were not available and for the polar solvents (acetone, chloroform and 1-butanol) whose parameter A^a was different from zero, the parameters were estimated by regression of vapor pressure experimental data, fixing the value of parameter A^a equal to zero.

For the calculation of copolymer parameters, the strategy adopted in previous works [21,22] for homopolymers, based on density calculations, could not be used since density data, as well as parameters for experimental correlations of density (such as the correlation of Tait [27]) are not available for copolymers. In this work, the pseudo-monomer concept proposed by Silva et al. [6] was used, the copolymer is considered formed by repeating units of pseudo-monomers, in which each co-monomer is represented weighted by its mole fraction in the copolymer. And so, there were defined combination rules for the parameters for the copolymer pseudo-monomer, from parameters found for the monomers of the homopolymers extracted from Lyrio et al. [22], weighted by the mole fraction of each monomer in the copolymer; in this way, the molecular weight of the group is calculated by:

$$MW^{psm} = x^{m_1} \cdot MW^{m_1} + x^{m_2} \cdot MW^{m_2} \tag{13}$$

where x is the mole fraction of each monomer in the pseudo-monomer group of the copolymer, calculated from the weight percent of each monomer in the copolymer. The supercripts psm, m_1 and m_2 are related to pseudo-monomer, monomer 1 and monomer 2, respectively.

For the hard-core volume, (v_∞^a) and area (Q^a) group parameters, arithmetic combination rules were used:

$$v_\infty^{psm} = x^{m_1} \cdot v_\infty^{m_1} + x^{m_2} \cdot v_\infty^{m_2} \tag{14}$$

$$Q^{psm} = x^{m_1} \cdot Q^{m_1} + x^{m_2} \cdot Q^{m_2} \tag{15}$$

For the interaction energy parameters between equal groups (u_0^{aa}/Ra and B^{aa}), geometric combination rules were used. However, special attention should be taken in this case, in order to conserve the parameter sign; u_0^{aa}/Ra is always negative and B^{aa} may be either negative or positive:

$$\frac{u_0^{psm\,psm}}{R} = -\left(x^{m_1} \cdot \left|\frac{u_0^{m_1 m_1}}{R}\right|^{1/2} + x^{m_2} \cdot \left|\frac{u_0^{m_2 m_2}}{R}\right|^{1/2}\right)^2 \tag{16}$$

$$B^{psm\,psm} = sm(si(B^{m_1 m_1})x^{m_1} \cdot |B^{m_1 m_1}|^{1/2}$$
$$+ si(B^{m_2 m_2}) \cdot x^{m_2} \cdot |B^{m_2 m_2}|^{1/2})^2 \tag{17}$$

where the symbol 'si' means the sign of the parameter and 'sm' is the sign of the highest value parameter in modulus.

3. The PC-SAFT equation of state

The original PC-SAFT EoS [23] considers that spherical segment chains of same type are composed by regular components and polymers. This molecular model is extended to copolymers [24] allowing different segment types (segments type α and β) in the molecular chain. The segment number $m_{i,\alpha}$ of same type α is obtained from pure-component parameter $(m/MW)_{i,\alpha}$, then:

$$m_{i,\alpha} = w_{i,\alpha} MW_{copolym}\left(\frac{m}{MW}\right)_{i,\alpha} \tag{18}$$

where $MW_{copolym}$ is the total molecular weight of copolymer, $w_{i,\alpha}$ is the weight fraction of repeated unit α and $(m/MW)_{i,\alpha}$ is the number of segments of type α per mass of α-monomer. The total number of molecular segments, m_i of copolymer i, is the sum of all segments, according to:

$$m_i = \sum_\alpha m_{i,\alpha} \tag{19}$$

The segment fraction $z_{i,\alpha}$ is given by:

$$z_{i,\alpha} = \frac{m_{i,\alpha}}{m_i} \tag{20}$$

For the specific case of a copolymer with statistical distribution of repeated units, the bonding fractions $B_{i\alpha,i\beta}$ can be determined from Table 1 [24].

Table 1
Bonding fractions $B_{i\alpha,i\beta}$ for a copolymer i containing segments α and β

Copolymer	Composition of the repeated unit	$B_{i\alpha,i\beta}$	$B_{i\alpha,i\alpha}$	$B_{i\beta,i\beta}$
Random	$z_{i,\beta} < z_{i,\alpha}$	$2[(z_{i,\beta}\, m_i)/(m_i-1)]$	$1 - B_{i\alpha,i\beta} - B_{i\beta,i\alpha}$	0
Random	$z_{i,\beta} > z_{i,\alpha}$	$2[(z_{i,\alpha}\, m_i)/(m_i-1)]$	0	$1 - B_{i\alpha,i\beta} - B_{i\beta,i\alpha}$
Alternating	$z_{i,\beta} = z_{i,\alpha}$	1	0	0

The PC-SAFT EoS is based on a reference hard-sphere chain term and a perturbation contribution term,

$$\tilde{a}^{\text{res}} = \tilde{a}^{\text{hc}} + \tilde{a}^{\text{pert}} \tag{21}$$

where $\tilde{a} = A/NkT$ and k is the Boltzmann constant. The hard-chain contribution [28] was based on the first-order thermodynamic perturbation theory [29–31]:

$$\tilde{a}^{\text{hc}} = \bar{m}\tilde{a}^{\text{hs}} - \sum_{i=1}^{n_c} x_i(m_i - 1) \sum_{\alpha}\sum_{\beta} B_{i\alpha,i\beta} \cdot \ln g_{i\alpha,i\beta(d_{i\alpha,i\beta})}^{\text{hs}} \tag{22}$$

where m is the segment number, x the mole fraction and $g_{i\alpha,i\beta(d_{i\alpha,i\beta})}^{\text{hs}}$ is the radial pair distribution function which takes in account the interactions between segments α and β, being defined as:

$$g_{i\alpha,i\beta(d_{i\alpha,i\beta})}^{\text{hs}} = \frac{1}{1-\xi_3} + \left(\frac{d_{i\alpha}d_{j\beta}}{d_{i\alpha}+d_{j\beta}}\right)\frac{3\xi_2}{(1-\xi_3)^2}$$
$$+ \left(\frac{d_{i\alpha}d_{j\beta}}{d_{i\alpha}+d_{j\beta}}\right)^2 \frac{2\xi_2^2}{(1-\xi_3)^3} \tag{23}$$

and $\bar{m}$ is the arithmetic average of the segment number, calculated as:

$$\bar{m} = \sum_{i=1}^{n_c} x_i m_i \sum_{\alpha} z_{i,\alpha} = \sum_{i=1}^{n_c} x_i m_i \tag{24}$$

The contribution of hard-sphere, $\tilde{a}^{\text{hs}}$, depends on the auxiliary variable ξ_k ($k=0$–3) and ξ depends on temperature dependent segment number, d and the total number density of molecules, ρ, thus:

$$\xi_k = \frac{\pi}{6}\rho\sum_{i=1}^{n_c} x_i m_i \sum_{\alpha} z_{i\alpha}d_{i\alpha}^k, \quad k = 0, 1\text{–}3 \tag{25}$$

where $d_{i\alpha}$ is referred to segment α and is calculated as

$$d_{i\alpha} = \sigma_{i\alpha}\left[1 - 0.12\exp\left(-\frac{3\varepsilon_{i\alpha}}{kT}\right)\right] \tag{26}$$

The perturbation contribution [32] is predicted from the first-order ($\tilde{a}_1$) and second-order ($\tilde{a}_2$) perturbation terms:

$$\tilde{a}^{\text{pert}} = \tilde{a}_1 + \tilde{a}_2 \tag{27}$$

where $\tilde{a}_1$ and $\tilde{a}_2$ depend on the total number density of molecules, ρ, the average of the segment number, $\bar{m}$, and the reduced density, η, and are expressed by VDW mixing rules (one fluid) represented as:

$$\tilde{a}_1 = -2\pi\rho\left(\sum_{k}^{6} a_k(\bar{m})\eta^k\right)\sum_{i=1}^{n_c}\sum_{j=1}^{n_c} x_i x_j m_i m_j$$
$$\times \sum_{\alpha}\sum_{\beta} z_{i\alpha}z_{j\beta}\left(\frac{\varepsilon_{i\alpha,j\beta}}{kT}\right)\sigma_{i\alpha,j\beta}^3. \tag{28}$$

$$\tilde{a}_2 = -\pi\rho\bar{m}\left(1 + Z^{\text{hc}} + \rho\frac{\partial Z^{\text{hc}}}{\partial\rho}\right)^{-1}\left(\sum_{k}^{6} b_k(\bar{m})\eta^k\right)$$
$$\times \sum_{i=1}^{n_c}\sum_{j=1}^{n_c} x_i x_j m_i m_j \sum_{\alpha}\sum_{\beta} z_{i\alpha}z_{j\beta}\left(\frac{\varepsilon_{i\alpha,j\beta}}{kT}\right)^2\sigma_{i\alpha,j\beta}^3 \tag{29}$$

where

$$1 + Z^{\text{hc}} + \rho\frac{\partial Z^{\text{hc}}}{\partial\rho} = 1 + \bar{m}\frac{8\eta - 2\eta^2}{(1-\eta)^4} + (1-\bar{m})$$
$$\times \frac{20\eta - 27\eta^2 + 12\eta^3 - 2\eta^4}{[(1-\eta)(2-\eta)]^2} \tag{30}$$

$$a_k(\bar{m}) = a_{0k} + \left(\frac{\bar{m}-1}{\bar{m}}\right)a_{1k} + \left(\frac{\bar{m}-1}{\bar{m}}\right)\left(\frac{\bar{m}-2}{\bar{m}}\right)a_{2k} \tag{31}$$

$$b_k(\bar{m}) = b_{0k} + \left(\frac{\bar{m}-1}{\bar{m}}\right)b_{1k} + \left(\frac{\bar{m}-1}{\bar{m}}\right)\left(\frac{\bar{m}-2}{\bar{m}}\right)b_{2k} \tag{32}$$

In equations above, Z^{hc} is the hard-chain compressibility factor, while the constants a_{ik} and b_{ik} were fitted with termophysical properties of pure n-alkanes [23]. Conventional combining rules are used to determine the cross parameters:

$$\sigma_{i\alpha,i\beta} = \frac{1}{2}(\sigma_{i\alpha} + \alpha_{i\beta}), \qquad \varepsilon_{i\alpha,i\beta} = \sqrt{\varepsilon_{i\alpha}\varepsilon_{i\beta}}(1 - \kappa_{i\alpha,i\beta}) \tag{33}$$

where $\varepsilon_{i\alpha i\beta}$ is the parameter that regards the segment–segment interactions and m, σ and ε are the PC-SAFT pure-component parameters of each segment.

The required parameters for a binary mixture, which is composed by poly(α-co-β) plus a solvent, are the three pure-component parameters of solvent, poly(α) and poly(β). Furthermore, three binary interaction parameters can be used. Two of these describe the polymer–solvent interactions and the third interaction parameter accounts for interactions between poly(α) and poly(β) segments within the copolymer, according to Eq. (33).

The final form for the fugacity coefficient for the model is:

$$\ln\hat{\phi}_i = \frac{\hat{\mu}_{i(T,V)}^{\text{res}}}{kT} - \ln Z \tag{34}$$

$$\frac{\hat{\mu}_{i(T,V)}^{\text{res}}}{kT} = \tilde{a}^{\text{res}} + (Z - 1) + \left(\frac{\partial\tilde{a}^{\text{res}}}{\partial x_i}\right)_{T,V,x_{j\neq i}}$$
$$- \sum_{j=1}^{n_c}\left[x_j\left(\frac{\partial\tilde{a}^{\text{res}}}{\partial x_j}\right)_{T,V,x_{k\neq j}}\right] \tag{35}$$

where $\hat{\mu}_i$ is the chemical potential of component i in the mixture.

When associating compounds are used, it is necessary to add a term to Eq. (21) in order to take in account the contribution due to association ($\tilde{a}^{\text{assoc}}$), which is given by:

$$\tilde{a}^{\text{assoc}} = \sum_{i=1}^{n_c} x_i \sum_{A_i}\left(\ln X_{A_i} - \frac{1}{2}X_{A_i} + \frac{1}{2}\right) \tag{36}$$

where X_{A_i} is the fraction of A-sites on molecule that do not form associating bonds with others active sites. This number is found through the solution of the non-linear system of equations:

$$X_{A_i} = \frac{1}{1 + N_A \sum_{j=1}^{n_c} \rho_j \sum_{B_j} X_{B_j} \varXi^{A_i B_j}} \tag{37}$$

where ρ_j is the molar density of component j, $\varXi^{A_i B_j}$ a function of the associating volume, $k^{A_i B_j}$, the associating energy, $\varepsilon^{A_i B_j}$, and the radial distribution function, $g_{(d+)}^{hs}$ [see Eq. (23)] and is defined as follows:

$$\varXi^{A_i B_j} = \sigma_{ij}^3 g_{(d+)}^{hs} \kappa^{A_i B_j} \left[\exp\left(\frac{\varepsilon^{A_i B_j}}{kT}\right) - 1 \right] \tag{38}$$

where $\varXi^{A_i B_j}$ measures the associating strength between site A on molecule i and site B on molecule j.

4. Vapor–liquid equilibrium calculations

Because copolymers are not volatile, the phase equilibrium conditions for binary copolymer–solvent mixtures can be given by:

$$x_1 \hat{\phi}_{1(T,P,x_i)}^L = \phi_{1(T,P,y_1=1)}^V \tag{39}$$

where x and y are the mole fractions in liquid and vapor phase, respectively, $\hat{\phi}_i$ the fugacity coefficient of the component in solution, ϕ_i the fugacity coefficient of pure component and "1" refers to the solvent. The fugacity coefficients were calculated by Eq. (10) [LGT EoS] and Eq. (34) [PC-SAFT EoS].

5. Results and discussion

The phase behavior of nine copolymer + solvent systems was studied at several compositions of the monomer-units of copolymer, using the PC-SAFT and the LGT Eos as thermodynamic models. Table 2 describes the main physical characteristics of the copolymer + solvent systems studied in this work. It is important to notice the nomenclature of copolymer names: the capital letters represent the copolymer name (composed by two monomer-units) and the number is the weight percent of the first monomer-unit.

Assumptions shown in Table 1 were applied in this work to the modeling of the random copolymers with a statistical distribution of repeat units α and β, and Table 3 displays the PC-SAFT characteristic parameters (segment and bonding fractions) of the copolymers in mixtures with solvents.

In Table 4, the LGT and PC-SAFT pure-component parameters are presented. On the left side there are shown the four parameters for solvents and monomers of the LGT EoS. On the right side there are shown the three pure-component parameters for solvents, monomers and polymers for the PC-SAFT EoS. Vapor pressure and liquid saturated volume data were used to calculate the solvent parameters, while liquid PVT data were

Table 2
Main physical characteristics of copolymer + solvent systems

Solvent	Copolymer[a]	n_p	w_1[b]	Temperature (K)	Pressure (MPa)	References
ACE	PSBR5	15	0.0003–0.1200	323.15	0.0137–0.0613	
	PSBR23	22	0.0090–0.2310	323.15–333.15	0.0127–0.0979	[1]
	PSBR45	24	0.0040–0.2580		0.0127–0.0979	
nC_4OH	PVAE9	7	0.0060–0.0360	353.15	0.0027–0.0152	
	PVAVC12	7	0.0070–0.0460		0.0027–0.0152	[1]
CHL	PVAE9	9	0.0310–0.2530	333.15	0.0140–0.0871	
	PVAE25	8	0.0620–0.4810		0.0139–0.0793	
	PVAE50	8	0.0980–0.5520		0.0139–0.0793	[1]
	PVAE70	8	0.0590–0.5730		0.0139–0.0793	
cC_6	PSBR5	9	0.0270–0.3230	333.15	0.0048–0.0407	
	PSBR23	15	0.0150–0.3280	296.65–333.15	0.0020–0.0407	[1]
	PSBR41	8	0.2169–0.4766	343.15	0.0472–0.0664	[33,34]
	PSBR45	16	0.0110–0.3010	296.65–333.15	0.0020–0.0407	[1]
cC_6	PVAE25	9	0.0110–0.3690	353.15	0.0075–0.0704	
	PVAE50	9	0.0050–0.2870		0.0075–0.0704	[1]
	PVAE70	9	0.0040–0.2420		0.0075–0.0704	
BZN	PSBR4.1	20	0.0459–0.4297	298.15–308.15	0.0022–0.0172	[35]
TOL	PSBR5	6	0.0430–0.5130	308.15	0.0009–0.0055	
	PSBR23	6	0.0290–0.0380		0.0009–0.0055	[1]
	PSBR41	16	0.1832–0.5692	343.15–373.15	0.0158–0.0677	[33,34]
nC_6	PSBR23	6	0.0140–0.2620	343.15	0.0139–0.0752	
	PSBR45	6	0.0160–0.2490		0.0139–0.0752	[1]
nC_5	PSBR23	9	0.0080–0.0890	333.15	0.0228–0.1376	
	PSBR45	6	0.0100–0.0340		0.0228–0.1376	[1]

[a] Numbers are for weight percent of first monomer.
[b] w_1: solvent weight fraction in copolymer phase.

Table 3
PC-SAFT parameters of the copolymers in mixtures with solvents

Bimary systems: Solvent+	MW copolymer	Copolymer composition wt% of constituent β	Segment fraction $z_{i\beta}$	Bonding fraction		
				$B_{i\alpha,i\alpha}$	$B_{i\alpha,j\beta}$	$B_{j\beta,j\beta}$
	100000	4.10[d] of PS	–	–	–	–
	100000	5.00[d] of PS	–	–	–	–
PSBR[a]	720000	23.00[e] of PS	0.1409	0.7161	0.2839	0.0000
	100000	41.00[d] of PS	–	–	–	–
	600000	45.00[f] of PS	0.3100	0.3707	0.6293	0.0000
	100000	9.00[g] of PVA	0.0802	0.8392	0.1608	0.0000
PVAE[b]	88000	25.00[h,i,j] of PVA	0.2271	0.5423	0.4577	0.0000
	250000	50.00[j] of PVA	0.4686	0.0487	0.9513	0.0000
	280000	70.00[j] of PVA	0.6729	0.0000	0.4633	0.5367
PVAVC[c]	30000	12.00[a] of PVA	–	–	–	–

[a] Solvents are ACE, cC$_6$, BZN, TOL, nC$_5$ and nC$_6$.
[b] Solvents are nC$_4$OH, CHL and cC$_6$.
[c] Solvent is nC$_4$OH.
[d] Copolymer PVT data not found in literature to be used in PC-SAFT EoS to calculate $\kappa_{i\alpha j\beta}$.
[e] Copolymer PVT data are taken from literature: [36].
[f] Copolymer PVT data are taken from literature: [37].
[g] Copolymer PVT data are taken from literature: [38].
[h] Copolymer PVT data are taken from literature: [39].
[i] Copolymer PVT data are taken from literature: [40].
[j] Copolymer PVT data are taken from literature: [41].

used to calculate the polymer parameters. It is important to notice that for associating compounds such as nC$_4$OH, there are two additional PC-SAFT pure-component parameters in order to correct the interaction molecules due to the associating forces.

In order to compare the two equations at the same basis, it was initially applied for both equations a methodology consisted of applying the concept of pseudo-monomers. Table 5 shows the pseudo-monomer parameters obtained for the two thermodynamic models which were calculated in accordance with Eqs. (13)–(15) by using the pure-component parameters of monomers and their compositions in the copolymer. The results, expressed as pressure deviations, together with interaction parameters for both thermodynamic models for this methodology, appear in Table 6. The pressure deviations were calculated according to:

$$\frac{\Delta P}{P} = \frac{100}{n_p} \sum_{i=1}^{n_p} \frac{|P_i^{calc} - P_i^{exp}|}{P_i^{exp}} \qquad (40)$$

where n_p represents the number of experimental points. In terms of global pressure deviations, the PC-SAFT EoS was capable of modeling vapor–liquid equilibrium of copolymer + solvent systems with more precision (4.41%) when compared with the results obtained with the LGT EoS (10.10%). These results are shown in Figs. 2–10, where solid lines are the correlated results obtained with the PC-SAFT EoS and dashed lines correspond to the correlated results obtained with the LGT EoS.

Fig. 2 shows a plot of pressure versus weight fraction of solvent in copolymer phase for acetone + poly(styrene-co-butadiene) at 323.15 and 333.15 K. The weight concentrations of styrene in styrene–butadiene copolymer are 5.00, 23.00 and 45.00%, respectively, and are represented as PSBR5, PSBR23 and PSBR45. Two binary interaction parameters for the LGT

EoS (B^{ba} and u_0^{ba}/R) and one binary interaction parameter (κ_{ij}) which takes in account the solvent + copolymer interactions for the PC-SAFT EoS of each acetone + PSBR system are shown in Table 6. With temperature independent binary parameters, good results can be obtained for the correlation of the VLE of acetone + PSBR systems, mainly with the PC-SAFT EoS.

Fig. 3 shows the comparison between calculated pressures and VLE experimental results [1] for 1-butanol + poly(vinyl acetate-co-ethylene) and 1-butanol + poly(vinyl acetate-co-vinyl chloride) systems at 353.15 K. Those are systems containing self-associating molecules. Adjusted binary interaction parameters for both EoS are shown in Table 6. From this table, it can be deduced that correlated results are in excellent
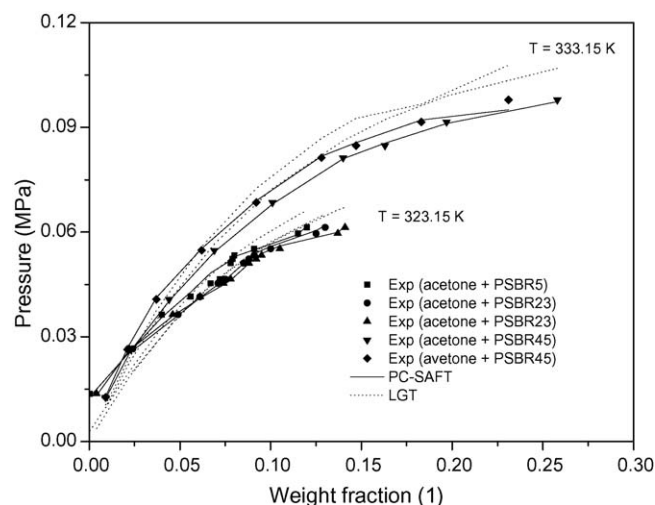

Fig. 2. VLE for ACE (1) + PSBR (2) systems at 323.15 and 333.15 K. Experimental data were taken from [1].

Table 4a
Pure-component parameters for LGT EoS

LGT EoS					
Groups	MW	v_∞^a (10^6 m^3/mol)	Q^a	B^{aa} (K)	u_0^{aa}/R (K)
Solvents					
nC_5[a]	72.15	25.613	3.0708	96.331	−604.796
nC_6[b]	86.18	27.284	3.4492	80.985	−679.584
cC_6[c]	84.16	22.923	2.5248	168.80	−705.286
BZN	78.12	37.975	4.5067	106.84	−507.720
TOL[d]	92.14	21.601	3.6697	108.28	−742.905
CHL[c]	119.38	22.048	4.1747	50.722	−642.003
ACE[d]	58.08	27.542	3.5557	111.73	−584.812
nC_4OH[d]	74.12	61.697	10.192	108.14	−385.077
Monomers					
STR[b]	104.14	82.074	8.5932	0.7607	−323.224
VA[b]	86.09	57.695	6.1134	5.3522	−249.269
BTD[b]	54.10	48.334	4.9983	6.4662	−231.991
ET[b]	28.10	30.520	3.1701	6.7838	−243.983
VC[b]	62.50	34.485	5.6125	−1.0051	−761.811

[a] [42].
[b] [22].
[c] [42].
[d] [43].

Table 4b
Pure component parameters for PC-SAFT EoS

	PC-SAFT EoS				
Solvents	m/MW (mol)$^{-1}$	σ (Å)	ε/k (K)	k^{AB}	ε^{AB} (K)
nC_5	0.034090	3.8729	240.11	–	–
nC_6	0.034088	3.8383	239.57	–	–
cC_6	0.029946	3.8399	279.21	–	–
BZN	0.032712	3.5878	281.55	–	–
TOL	0.030984	3.6869	282.69	–	–
CHL	0.021826	3.4085	265.94	–	–
ACE	0.037879	3.4956	272.26	–	–
nC_4OH	0.035126	3.7563	263.18	0.008752	2489.23
Monomers					
STR	0.024339	3.9750	318.70	–	–
VA	0.011525	5.0706	421.42	–	–
BTD	0.046033	3.4508	215.10	–	–
ET	0.056070	3.4250	178.77	–	–
VC	0.091211	2.4024	160.05	–	–
Polymers					
PS[a]	0.033238	3.5022	320.14	–	–
PVA[a]	0.029905	3.5086	310.14	–	–
PB[a]	0.060552	2.9845	240.21	–	–
PE[a]	0.028193	4.0125	320.24	–	–
PVC[a]	0.021369	3.7486	370.42	–	–

[a] [44].

agreement with the experimental data [1] for those associating systems; in terms of pressure deviations, the LGT EoS has the lower deviations for both systems.

The results for chloroform + poly(vinyl acetate-*co*-ethylene) systems at 333.15 K for different weight percent of vinyl acetate in vinyl acetate–ethylene copolymers (9.00, 25.00, 50.00 and 70.00%) are shown in Fig. 4. VLE for these systems was correlated by adjusting binary interaction parameters, which are shown in Table 6 for each EoS. In a quantitative way, the pres-

sure deviations obtained with PC-SAFT EoS are lower when compared with those obtained with the LGT EoS.

Fig. 5 shows the comparison between calculated pressures and experimental results [1,33,34] for cyclohexane + poly(styrene-*co*-butadiene) systems at 296.65, 333.15 and 343.15 K for several weight percent of styrene in styrene–butadiene copolymers (5.00, 23.00, 41.00 and 45.00%). Two adjustable parameters (B^{ba} and u_0^{ba}/R) for the LGT EoS and one adjustable parameters (κ_{ij}) which measures the sol-

Table 5
Pseudo-monomer parameters for LGT and PC-SAFT EoS

Copolymer	LGT EoS				PC-SAFT EoS		
	v_∞^a (10^6 m^3/mol)	Q^a	B^{aa} (K)	u_0^{aa}/R (K)	m/MW (mol)$^{-1}$	σ (Å)	ε/k (K)
PSBR4.1	49.067	5.0764	6.2829	−233.813	0.045562	3.4622	217.35
PSBR5	49.232	5.0940	6.2421	−234.223	0.045456	3.4647	217.86
PSBR23	52.866	5.4811	5.3754	−243.367	0.043119	3.5212	229.01
PSBR41	57.283	5.9518	4.4088	−254.720	0.040280	3.5898	242.57
PSBR45	58.396	6.0704	4.1805	−257.620	0.039562	3.6072	246.00
PVAE9	31.368	3.2620	6.7365	−244.147	0.054676	3.4765	186.36
PVAE25	33.182	3.4584	6.6361	−244.498	0.051700	3.5864	202.57
PVAE50	37.198	3.8934	6.4163	−245.277	0.045107	3.8300	238.49
PVAE70	42.257	4.4413	6.1447	−246.259	0.036813	4.1364	283.67
PVAVC12	36.576	5.6576	0.4954	−704.204	0.084039	2.6425	183.57

vent + copolymer interactions for the PC-SAFT EoS are determined by fitting VLE data of each cyclohexane + poly(styrene-*co*-butadiene) system at constant temperature; these parameters are in Table 6. PC-SAFT pressure deviations are lower than the pressure deviations obtained with the LGT EoS.

Fig. 6 compares VLE data experimental [1] for poly(vinyl acetate-*co*-ethylene) + cyclohexane systems at 353.15 K for different weight percent of vinyl acetate in vinyl acetate–ethylene copolymers (25.00, 50.00 and 70.00%) with calculated results obtained with the LGT and PC-SAFT models. The binary interaction parameters are shown in Table 6. Correlated

results obtained with the PC-SAFT EoS are in better agreement than ones obtained with the LGT EoS when are compared in terms of pressure deviations with experimental data [1].

Figs. 7 and 8 compare VLE data for poly(styrene-*co*-butadiene) and poly(styrene-*co*-butadiene) for two weight percent of styrene in styrene–butadiene copolymers (23.00 and 45.00%) in pentane (at 333.15 K) and hexane (at 343.15 K) with calculated results, respectively. The binary interaction parameters for each thermodynamic model are shown in Table 6. The correlated results in terms of pressure deviations are in good

Table 6
Results obtained for the modeling of copolymer + solvent systems using the first methodology

| Solvent	Copolymer	LGT			PC-SAFT	
		B^{ba} (K)	u_0^{ba}/R (K)	$\Delta P/P$ (%)	κ_{ij}	$\Delta P/P$ (%)
ACE	PSBR5	34.080	−373.500	10.53	0.0120	4.78
	PSBR23	−1.0193	−422.469	7.18	0.0122	3.04
	PSBR45	−57.066	−521.866	10.32	0.0130	5.19
nC$_4$OH	PVAE9	81.008	−307.931	3.82	0.0230	4.05
	PVAVC12	53.452	−496.475	4.20	−0.0126	5.18
CHL	PVAE9	32.860	−442.43	7.07	−0.1208	4.18
	PVAE25	35.057	−470.868	16.86	−0.0816	5.06
	PVAE50	36.124	−486.782	16.23	−0.0701	4.41
	PVAE70	35.976	−489.007	26.73	−0.0516	3.28
cC$_6$	PSBR5	51.596	−430.131	15.72	0.0118	3.66
	PSBR23	−27.743	−538.326	12.72	0.0104	4.38
	PSBR41	50.592	−418.634	6.74	0.0088	2.28
	PSBR45	−47.915	−596.968	12.51	0.0101	4.31
cC$_6$	PVAE25	6.1817	−481.450	7.51	−0.1068	5.36
	PVAE50	6.0434	−471.136	12.13	−0.0858	6.90
	PVAE70	5.9136	−469.771	11.04	−0.0636	5.73
BZN	PSBR4.1	93.240	−313.260	4.92	0.0202	2.44
TOL	PSBR5	63.981	−450.566	3.37	0.0080	4.07
	PSBR23	69.172	−448.891	3.31	0.0091	5.76
	PSBR41	−52.602	−677.198	7.59	0.0098	3.71
nC$_6$	PSBR23	35.724	−395.208	12.21	0.0086	3.92
	PSBR45	42.548	−394.415	11.33	0.0089	4.28
nC$_5$	PSBR23	45.408	−336.736	6.84	0.0072	3.68
	PSBR45	42.886	−315.799	11.49	0.0079	6.24
Global pressure deviation				10.10		4.41
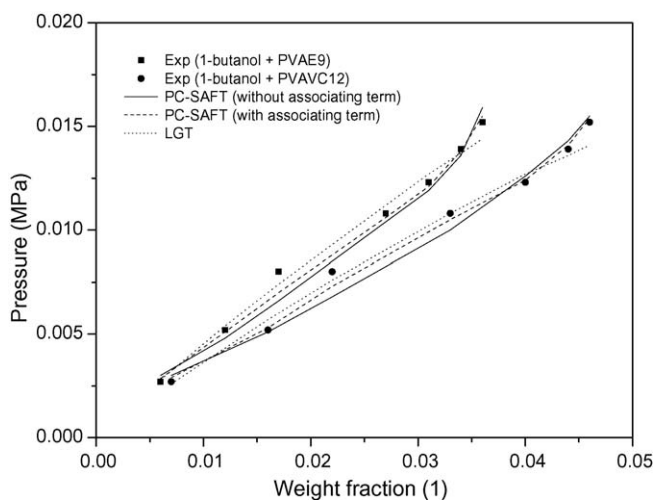
Fig. 3. VLE for nC$_4$OH (1) + PVAE (2) and nC$_4$OH + PVAVC systems at 353.15 K. Experimental data were taken from [1].
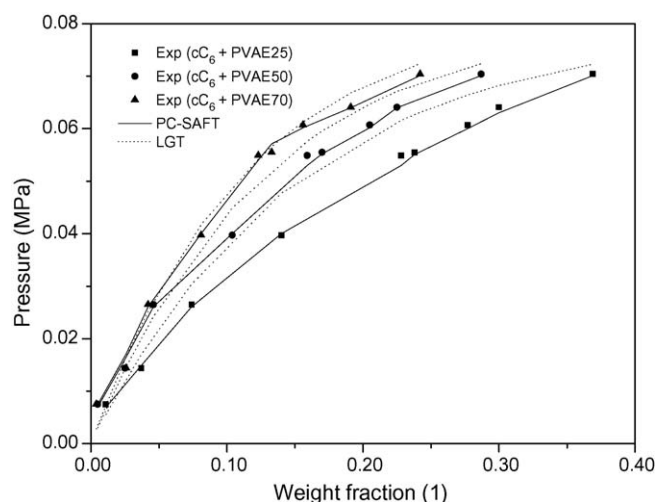

Fig. 6. VLE for cC$_6$ (1) + PVAE (2) systems at 353.15 K. Experimental data were taken from [1].
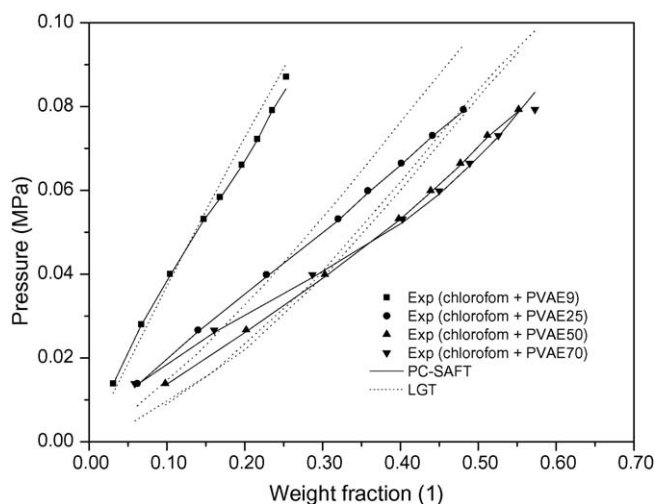

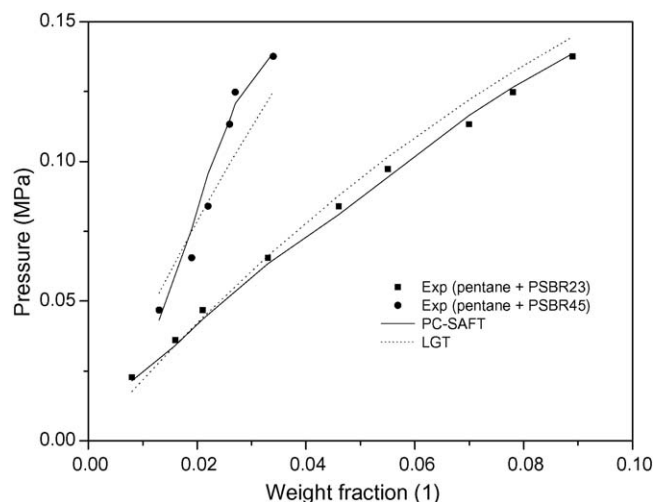Fig. 4. VLE for CHL (1) + PVAE (2) systems at 333.15 K. Experimental data were taken from [1].

Fig. 7. VLE for nC$_5$ (1) + PSBR (2) systems at 333.15 K. Experimental data were taken from [1].
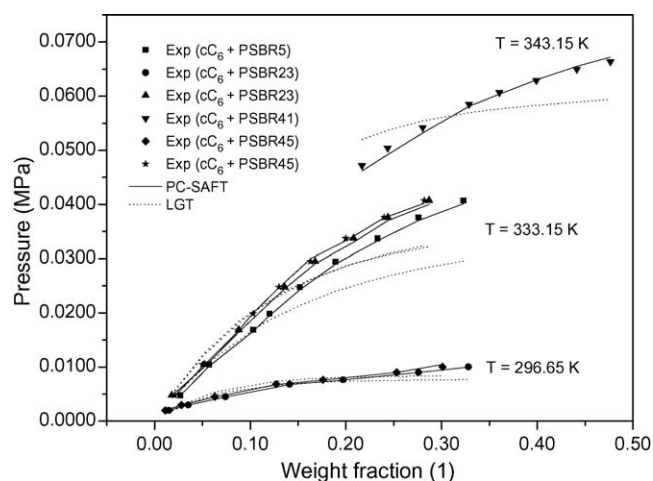

Fig. 5. VLE for cC$_6$ (1) + PSBR (2) systems at 296.65, 333.15 and 343.15 K. Experimental data were taken from [1,33,34].
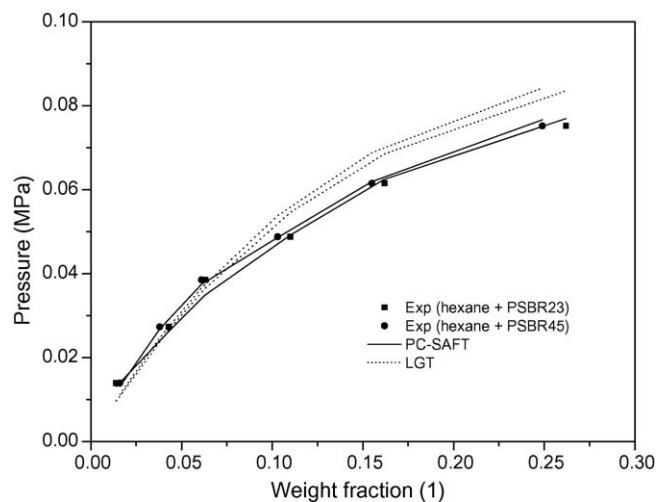

Fig. 8. VLE for nC$_6$ (1) + PSBR (2) systems at 343.15 K. Experimental data were taken from [1].
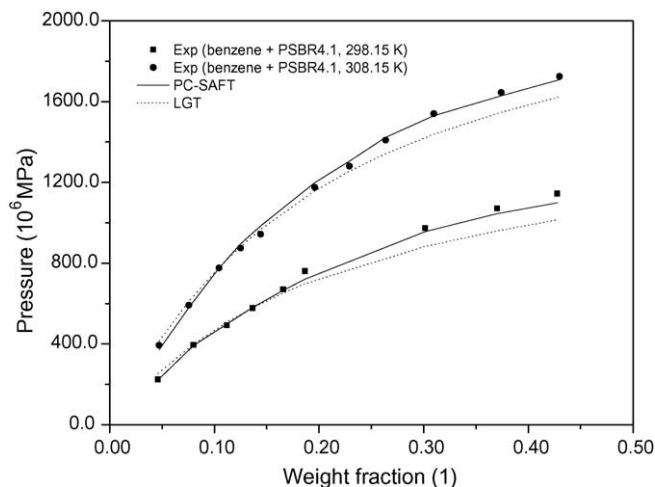
Fig. 9. VLE for BZN (1) + PSBR (2) systems at 298.15 and 308.15 K. Experimental data were taken from [33,34].

agreement with the experimental data [1]; the lowest pressure deviations obtained with the PC-SAFT EoS.

VLE results of benzene + poly(styrene-*co*-butadiene) systems at 298.15 and 308.15 K obtained with the LGT and PC-SAFT models are compared with experimental data [33,34] in Fig. 9. Weight percent of styrene in styrene–butadiene copolymer is constant and equal to 4.10%. Binary interaction parameters for each EoS can be seen in Table 6. According to pressure deviations presented in Table 6, it can be noticed that PC-SAFT EoS has better performance than LGT EoS.

VLE for toluene + poly(styrene-*co*-butadiene) systems is modeled at several temperatures (308.15, 343.15 and 373.15 K) for copolymers with two different content of styrene in styrene–butadiene copolymers (5.00 and 41.00% in weight fraction); the results are shown in Fig. 10. Adjustable interaction parameters were obtained by correlating the experimental data [1,33,34], and they are presented in Table 6. In terms of pressure deviations, both EoS have similar performance.

In order to have a more realistic correlation for vapor–liquid equilibrium for these systems, the parameters were also adjusted
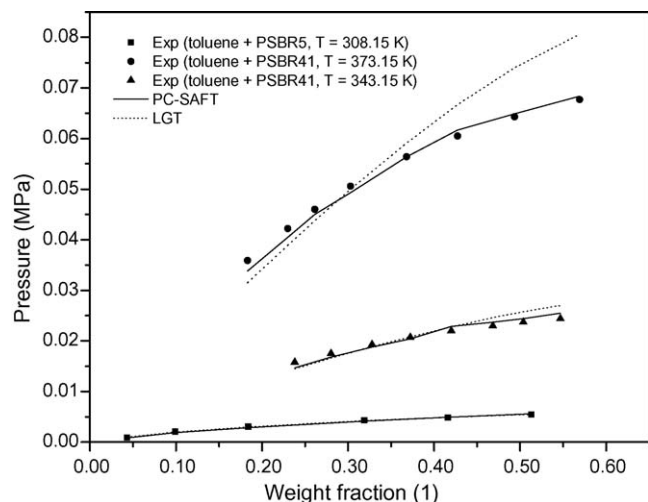
considering each co-monomer in the solution. And so, it was used a second methodology consisted in adjusting simultaneously the binary interaction parameters to one family of copolymers with a solvent, taking in account that for the interactions between each monomer-unit with a solvent it is necessary to adjust only one interaction parameter and for the interactions between monomer-units it is necessary to adjust several interaction parameters, depending on the compositions between them on the copolymer chain. As this methodology leads to different numbers of parameters in each equation, the comparison was not done in this case and it was only studied the PC-SAFT EoS, which described the vapor–liquid phase behavior better than the LGT EoS with the first methodology used. In PC-SAFT EoS, the binary parameters take in account the interactions between solvent + monomer 1 (k_{ij}^a) and solvent + monomer 2 (k_{ij}^b), while $k_{ia,jb}$ represents the binary interaction parameter which takes in account the interaction between the two monomer-units of copolymer. In terms of global pressure deviations of all systems studied in this work, the pressure deviations obtained for the PC-SAFT EoS was 2.04%. A complete list of pressure deviations for each copolymer + solvent system is shown in Table 7.

Table 7
PC-SAFT results obtained for the modeling of copolymer + solvent systems using the second methodology

Solvent	Copolymer	PC-SAFT			
		κ_{ij} [a]	κ_{ij} [b]	$\kappa_{i\alpha j\beta}$ [c]	$\Delta P/P$ (%)
ACE	PSBR5	0.0121	0.0028	0.0003	2.83
	PSBR23			0.0004	
	PSBR45			0.0001	
nC$_4$OH	PVAE9	0.0160	0.0131	−0.0010	1.88
	PVAVC12	−0.0101	−0.0090	0.0008	1.63
CHL	PVAE9	−0.0532	0.0003	0.0008	2.59
	PVAE25			0.0005	
	PVAE50			0.0003	
	PVAE70			0.0003	
cC$_6$	PSBR5	0.0052	0.0012	0.0008	2.11
	PSBR23			0.0006	
	PSBR41			0.0005	
	PSBR45			0.0002	
cC$_6$	PVAE25	−0.1085	0.0101	0.0011	2.09
	PVAE50			0.0010	
	PVAE70			0.0008	
BZN	PSBR41	0.0186	0.0109	0.0004	1.23
TOL	PSBR5	0.0082	0.0126	0.0014	2.13
	PSBR23			0.0011	
	PSBR41			0.0006	
nC$_6$	PSBR23	0.0080	0.0091	0.0010	1.84
	PSBR45			0.0008	
nC$_5$	PSBR23	0.0066	0.0108	0.0013	2.07
	PSBR45			0.0008	
Global pressure deviation					2.04

[a] Binary interaction parameter: solvent–monomer 1.
[b] Binary interaction parameter: solvent–monomer 2.
[c] Binary interaction parameter: monomer 1–monomer 2.

Fig. 10. VLE for TOL (1) + PSBR (2) systems at 308.15, 343.15 and 373.15 K. Experimental data were taken from [1,33,34].

6. Conclusions

Two theoretical EoS, LGT and PC-SAFT, are used to model VLE of 24 solvent + copolymer systems. There were used two methodologies. The first one was used by applying the pseudo-monomer concept; results obtained with this method show that PC-SAFT pressure calculations are in better agreement with experimental data than the ones obtained by the LGT EoS. The second methodology consisted in adjusting simultaneously the binary interaction parameters to one family of copolymers with a solvent, taking in account that, for the interactions between each monomer-unit with a solvent, it is necessary to adjust only one interaction parameter and, for the interactions between monomer-units, it is necessary to adjust several interaction parameters, depending on the composition of monomer-units on the copolymer chain. The second methodology appears to be the best method because it maintains the copolymer concept, where the copolymers are composed of different monomer-units; the global pressure deviations obtained in the second method by the PC-SAFT EoS were lower than those obtained in the first method. In both methods, the monomer–monomer interaction parameter depends on the composition of monomer-units in the copolymers.

List of symbols

$\tilde{a}$	Helmholtz free energy
A	Helmholtz free energy
B	bonding fractions
d	temperature-dependent segment diameter
EoS	equation of state
g	radial pair distribution function
k	Boltzmann constant
LGT	lattice gas theory
m	segment number
$\bar{m}$	average segment number
MW	molecular weight
n	mole number
n_c	component number
n_g	number of segments
n_p	experimental point data
N	total number of molecules
P	system pressure
PC-SAFT	perturbed chain-statistical associating fluid theory model
PVT	pressure–volume–temperature
R	ideal gas constant
T	absolute temperature
v	molar volume
V	volume
VDW	van der Waals
w	weight fraction
x	mole fraction in liquid phase
X_A	fraction of A-sites on molecule that do not form associating bonds
y	mole fraction in vapor phase
z	segment fraction
Z	compressibility factor
Z_C	coordination number

Greek letters

α, β	repeated units of monomers
ε	interaction energy parameter
$\hat{\phi}$	fugacity coefficient
η	reduced density
κ	adjustable temperature-dependent binary interaction parameter
μ	chemical potential
π	constant
ρ	total number density of molecules; system density
σ	segment diameter
ξ	auxiliary variable
Δ	increment
Ξ	variable which measures the associating strength between sites

Superscripts

assoc	associating
calc	calculated
exp	experimental
hc	hard chain
hs	hard sphere
pert	perturbation
res	residual

Subscripts

copolym	copolymer
i, j	component
l, k	species
mix	mixture
R	reduced property

Acknowledgements

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