Desenvolvimento de uma equação cúbica de estado para a predição de equilíbrio líquido-vapor em soluções poliméricas

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Abstract

An alternative cubic equation of state (CEOS) is proposed based on temperature-pressure superposition principle. A generic CEOS form, with the Peng-Robinson parameters, is used and a temperature-dependent attractive term $a(T)$ is developed, allowing an easy calculation of thermodynamic properties and vapor-liquid equilibrium. The new equation is applied to pure polymer and polymer solutions and its predictions compared with those of two others equations of state. For polymer solutions, two mixing rules without binary interaction parameters were used. The vapor-liquid equilibrium (VLE) predictions show good agreement with experimental data as well as pressure-volume-temperature (PVT) behavior of polymer liquids, attesting the appropriate form of the new equation proposed.

Key words: cubic equations of state, polymer solution, polymer liquids, mixing rule

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1. Introduction

Cubic equations of state (CEOS) are widely used in engineering for computing phase equilibrium and thermodynamic properties of simple mixtures. Since van der Waals proposed the first version of his celebrated equation of state (EOS) more than a century ago, many modifications have been proposed in the literature to improve the predictions of volumetric, thermodynamic, and phase equilibrium properties. Although the van der Waals (vdW) equation is not accurate for most applications, it can be considered the major contribution to this field since the first attempts to represent pressure-volume-temperature (PVT) behavior made by Boyle in the 17th century (Valderrama, 2003).

The vdW equation and most of the many modifications that are now available are special cases of a generic cubic equation, which can be written as:

$$P = \frac{RT}{V-b} - \frac{a(T)}{(V+\epsilon b)(V+\sigma b)} \tag{1}$$

where ϵ and σ are constants for all substances and depend on the EOS (see Table 1) and $a(T)$ and b are, respectively, the attractive and co-volume parameters specific for each substance. These parameters are usually determined using generalized correlations based on critical properties and acentric factor, accordingly to:

$$a(T) = \Psi \frac{\alpha(T_r,\omega) R^2 T_c^2}{P_c} \tag{2}$$

$$b = \Omega \frac{RT_c}{P_c} \tag{3}$$

where T_c is the critical temperature, P_c is the critical pressure, ω is the acentric factor, $T_r = T/T_c$ the reduced temperature and the other symbols are shown in Table 1.

Table 1: Specific cubic equation parameters.

EOS	$\alpha(T_r)$	σ	ϵ	Ω	Ψ
vdW	1	0	0	1/8	27/64
RK	$T_r^{-1/2}$	1	0	0.08664	0.42748
SRK	$\alpha_{SRK}(T_r;\omega)^{\star}$	1	0	0.08664	0.42748
PR	$\alpha_{PR}(T_r;\omega)^{\star\star}$	$1+\sqrt{2}$	$1-\sqrt{2}$	0.07780	0.45724

$^{\star}\alpha_{SRK}(T_r;\omega) = \left[1 + (0.48 + 1.574\omega - 0.176\omega^2)\left(1 - T_r^{1/2}\right)\right]^2$

$^{\star\star}\alpha_{PR}(T_r;\omega) = \left[1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)\left(1 - T_r^{1/2}\right)\right]^2$

As can be seen in Table 1, the specific values of ϵ, σ, and/or $\alpha(T_r)$ are what differentiate one equation from another. In fact, variations in values or expressions for $a(T)$ and b are the source for hundreds of cubic EOS available today.

For most of the low molecular weight substances, the critical properties and acentric factor are easily found or can be determined in laboratory. However, for polymers and other macromolecules these data cannot be determined experimentally because the material degrades before reaching the critical point. To overcome this situation, it is very common to predict these parameters by using group contribution methods. Another alternative is the direct estimation of the $a(T)$ and b terms using pressure-volume-temperature (PVT) data, like in (Louli and Tassios, 2000; Zhong and Masuoka, 1996; Wang, 2007). Although the results with fitted a and b parameters are quite

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accurate, the range of its applicability is retrict to the range of the experimental data used in the estimation. Through the former methodology, the calculation is easier but the group parameters used are strongly dependent on the specific structural features of the molecules and are common for closely related compounds only.

The major part of the commercial softwares have an implementation of a cubic equation. Still, the introduction of excess Gibbs free energy (G^E) mixing rules extends the usability of cubic equations to strongly polar systems and very asymmetric mixtures like solvent-polymer and polymer-polymer.

Today, we have several works using CEOS to estimate pure polymer properties and the phase equilibrium of polymer solutions. In general, the results are reasonable but in the most of the times the use of empirical binary interaction parameters or another experimental adjustments is mandatory. The main disadvantage is that this kind of parameter is system- and temperature-dependent which limits the use of the equation to a narrow range of reliability.

In this work, the usual relations for $a(T)$ and b based on critical properties are replaced by an approximation based on the temperature-pressure superposition principle widely discussed in (Sanchez et al., 1993b,a; Sanchez and Cho, 1995). Based on these works, a temperature dependent expression to $a(T)$ is suggested. In this way, we tried to improve the pure component prediction using the forementioned works and extend its applicability to polymer solutions using a CEOS. For the parameter b an expression depending only on one universal parameter is used. As a consequence, a new cubic equation of state is proposed in which no critical properties or acentric factor are necessary, when reliable values for these parameters are not available.

Additionally, the use of the proposed EOS combined with excess Gibbs free energy (G^E) mixing rules which do not rely on empirical binary interaction parameters was tested. This methodology is expected to present the following advantages in the analysis of the thermodynamic properties of complex mixtures involving macromolecules:

- can be easily implemented in commercial softwares;
- can be used to predict the behavior of pure polymer liquid or polymer solutions;
- has a temperature dependent attractive term;
- does not require any binary interaction parameter.

To contextualize the developments and make clear the relevance of the equation proposed, a review with some of the important accomplishments in the last few years is shown in Section 2. After that, the new equation is proposed and the mixing rules used to extend the applicability of the equation to polymer solutions are presented in Section 3. The prediction of the pure liquid polymer behavior and the phase equilibrium in polymer solutions are compared with literature data and results found by (Sanchez and Cho, 1995; Danner and High, 1993; Wang, 2007) and (Louli and Tassios, 2000) in Section 4 and Section 5.

2. The current state of CEOS and its applications for polymer systems

Several equations of state have been proposed for solvent-polymer and polymer-polymer mixtures in the past few years. Besides the CEOS, which were discussed in Section 1 and are the basis of the developments in this work, the thermodynamic equations can be classified into two broad groups: lattice models and continuum models (Valderrama, 2003). As examples for the first group we can cite: cell models, lattice-fluid models, hole models and for the second group: models based on mechanical statistics (SAFT and PC-SAFT, for instance) and cubic equations of state (CEOS). The last one, CEOS, has the advantage of being largely used for simple components.

It seems that nearly all equations of state for polymer liquids provide reasonably good fit to PVT data, especially at low pressures. However, there is a major difference between the various equations in their capability to fit PVT data over a wide range of pressure and to predict thermodynamic properties of polymer blends and solutions, particularly phase separation behavior. Most equations require an empirical interaction parameter, determined from at least one experimental data point, in order to describe accurately the phase behavior (Rodgers, 1993).

In Sako et al. (1989), the authors used the van der Waals theory to propose a three parameter cubic EOS which is applicable to fluids containing small or large molecules, including polymers. The authors extended it to mixtures using simple mixing rules and reproduced high-pressure phase equilibria for the ethylene-polyethylene system with good results. In Orbey and Sandler (1994), using a different approach, the authors combined the SRK equation with the Flory-Huggins activity coefficient model in a Huron-Vidal EOS with a G^E mixing rule. They analyzed binary polystyrene-hydrocarbon solvent mixtures, obtaining acceptable results. Orbey et al. (1998) used a polymer SRK equation to correlate polyethylene-ethylene mixtures and compared the results with the Sanchez-Lacombe and SAFT calculations. Kalospiros and Tassios (1995) found satisfactory results with the use of a simplified Wong-Sandler mixing rule proposed by Zhong and Masuoka (1996) for alkane/alkane mixtures, alkane/polymer mixtures and polymer/solvent mixtures.

In Sanchez and Cho (1995), a semi-empirical equation of state was developed to describe pure polymer liquids behavior. This equation was based on the temperature-pressure superposition principle and on the empirical observation that for polymers liquids both density and the logarithm of the bulk modulus are linear functions of temperature. In this equation, each polymer is distinguished by a characteristic temperature T^*, pressure P^* and density ρ^* and its predictions approach the accuracy of experimental PVT data for pure polymer liquids.

Recently, Louli and Tassios (2000) proposed a new cubic equation. This equation is based on the Peng Robinson EOS with an intersting modification. They provided specified a and b values for different kinds of polymers and assumed that a/M and b/M are independent of molecular weight M. Likewise, Wang (2007) present a and b parameters for the Soave-Redlich-Kwong EOS. These equations provide satisfactory results for the PVT behavior of pure polymers but some systematic errors were found in isobaric tests due to the temperature-independent a term.

3. Methodology

3.1. A new CEOS for pure polymers and polymer solutions

The development of the new equation is as follows. Using the simple relation for the reduced density $\widetilde{\rho}_0 \equiv \rho_0/\rho^*$, derived from the forementioned principle in Sanchez and Cho (1995), we can write:

$$\widetilde{\rho}_0 \equiv \frac{\rho_0}{\rho^*} = 1 - \widetilde{T} \tag{4}$$

where $\widetilde{T} \equiv T/T^*$, ρ^* is a characteristic mass density and ρ_0 is the mass density at T and a reference pressure P_0. Solving the Equation 4, we obtain the molar volume at P_0:

$$v_0 = \frac{M}{\rho^*\left(1 - \widetilde{T}\right)} \tag{5}$$

From the generic form of the CEOS (Equation 1), we can isolate the $a\left(T\right)$ term:

$$a\left(T\right) = \left(\frac{RT}{v-b} - P\right)\left(v + \epsilon b\right)\left(v + \sigma b\right) \tag{6}$$

Considering low pressures, that is $P_0 = 0$ and as a consequence $v = v_0$, we can simplify the Equation 6 and define a new form for $a\left(T\right)$ to be used in CEOS's:

$$a\left(T\right) = \left(\frac{RT}{v_0 - b}\right)\left(v_0 + \epsilon b\right)\left(v_0 + \sigma b\right) \tag{7}$$

where v_0 is only a function of temperature as stated in Equation 5. Additionally, the co-volume parameter b is chosen as a function of the characteristic density ρ^* and the molecular weight M:

$$b = b_0 \frac{M}{\rho^*} \tag{8}$$

where b_0 is a universal constant for all polymers. Our investigation shows that the best value of b_0 is 1.17, when using PR. Different values for b_0 are expected for different values of ϵ and σ. In this work all results were obtained with ϵ and σ matching those of the PR equation of state.

The characteristic temperature T^* and characteristic mass density ρ^* can be estimated from pure polymer liquid PVT data. A list of T^* and ρ^* parameters for 61 different polymers is available in Sanchez and Cho (1995).

With the above development, the CEOS parameters $a(T)$ and b can be determined for polymers. When compared with the currently available CEOS, the pure polymer PVT behaviour is better approximated by the proposed methodology (Section 4). For the prediction of solvent-polymer VLE, good results are obtained using mixing rules from the literature even when no binary interaction parameters are used (Section 5).

3.2. Mixing Rules

When dealing with mixtures, the expressions for the attractive a and co-volume b term should be computed as a function of the pure substances values a_i and b_i through a mixing rule.

A general relationship between A^E and G_0^E (G^E extrapolated to zero pressure), can be derived from the definition of the excess Gibbs energy. Using this definition, the assumption that v^E is equal zero and that the packing fraction $1/u$ is constant, the following expression can be obtained:

$$\frac{A^E}{RT} - \frac{G_0^E}{RT} = \sum x_i ln \frac{b}{b_i} \tag{9}$$

For a detailed explanation of the development above, see Fischer and Gmehling (1996).

From a CEOS, we can find an expression for A^E/RT. This expression can be substituted in Equation 9 to get:

$$\frac{A^E}{RT} = A_0\left[\frac{a}{bRT} - \sum_i x_i \frac{a_i}{b_i RT}\right] = \frac{G_0^E}{RT} + \sum x_i ln \frac{b}{b_i} \tag{10}$$

where A_0 is a constant that depends on the EOS used. For example, A_0 is -0.5777 for PR and -0.6466 for SRK.

The G_0^E in Equation 9 and Equation 10 is the excess Gibbs free energy at zero pressure and is usually evaluated by a G^E model such as NRTL and UNIFAC.

Based on the equation above, several works have made empirical modifications in its form in order to improve the results obtained. In the Universal Mixing Rule (UMR) proposed by Voutsas et al. (2004) the authors coupled PR EOS with UNIFAC. To calculate the G^E, the Flory-Huggins contribution of the combinatorial part of the UNIFAC model was neglected as well as the $\sum x_i ln(b/b_i)$ term (also known as the EOS Flory-Huggings term – FH^{EOS}). The authors also stated that these terms are responsible for poor results in predicting the VLE for some systems. Thus, the UMR is as follows:

$$\frac{G^{E,SG} + G^{E,res}}{RT} = A_0\left[\frac{a}{bRT} - \sum_i x_i \frac{a_i}{b_i RT}\right] \tag{11}$$

where $G^{E,SG}$ is the Staverman-Guggenhein contribution of the combinatorial term of G^E and $G^{E,res}$ is the residual part of the UNIFAC Gibbs free energy expression.

To evaluate the co-volume parameter b, the following equation was used:

$$b = \sum_i \sum_j x_i x_j b_{ij} \qquad b_{ij} = \left(\frac{b_i^{\frac{1}{2}} + b_j^{\frac{1}{2}}}{2}\right)^2 \tag{12}$$

Alternatively to UMR, a formulation independent on the form of the G^E model, that is, irrespective if it has an explicit FH term or a combinatorial and residual part, was proposed by Staudt et al. (2009). This equation is shown bellow:

$$\frac{G^E}{RT} = A_0\left[\frac{a}{bRT} - \sum_i x_i \frac{a_i}{b_i RT}\right] \tag{13}$$

where G^E is evaluated by any Gibbs free energy without simplifications.

In this work, we refer to it as the universal and generic mixing rule (UGMR). The parameter b is also evaluated using Equation 12.

3.3. Equation parameters and experimental data

The characteristic parameters T^* and ρ^* necessary for the new equation are available for 61 different polymers in Sanchez and Cho (1995). For the polymers used here, the parameters are reproduced in Table 2:

Table 2: Characteristic parameters for polymer liquids taken from Sanchez and Cho (1995).

Polymer	Name	ρ^* (g/cm^3)	T^* (K)
PS	Polystyrene	1.2247	2277.2
PIB	Poly(isobutylene)	1.0659	2130.2
PEO	Poly(ethylene oxide)	1.3439	1789.1
PVAc	Poly(vinyl acetate)	1.4455	1696.0
PDMS	Poly(dimethyl siloxane)	1.2390	1375.1
PMMA	Poly(methyl metacrylate)	1.4007	2184.2
LDPE	Low density polyethylene	1.0150	1865.4

The outcomes obtained in this work were compared with the PR and SRK equations from Louli and Tassios (2000) and Wang (2007), called here PR-LT and SRK-W, respectively. In pure polymer PVT tests, instead of experimental data, we compared the results with the Universal Padé equation of state from Sanchez and Cho (1995). According to the authors the accuracy of this equation approaches the accuracy of experimental PVT data for polymer liquids.

The parameters a/M and b/M for the PR-LT and SRK-W equation for the polymers tested in these work are shown in Table 3 and Table 4 with its original units of measure.

Table 3: PR EOS parameters extracted from Louli and Tassios (2000).

Polymer	a/M $(cm^6 bar/molg)$	b/M (cm^3/g)
LDPE	1373984	1.1991
PS	1315409	0.9549
PVAc	1847343	0.8428
PMMA	1277496	0.8407
PIB	2307400	1.0882
PEO	2278342	0.9497
PDMS	1021986	0.9968

To describe phase equilibria in mixtures, methods of the type “EOS + Gibbs free energy” seem to be the most appropriate for modeling mixtures with highly asymmetric components (Valderrama, 2003). In this work, we have combined the proposed CEOS as well as PR-LT and SRK-W with UNIFAC. The UNIFAC implementation chosen here is as described by Horstmann et al. (2005) with three parameters for the temperature dependent parameter Ψ_{mn}:

Table 4: SRK EOS parameters from Wang (2007).

Polymer	a/M $(m^6 Pa/molg)$	b/M (dm^3/g)
PS	0.02998	1.0224E-03
PIB	0.0276	0.9400E-03
PEO	0.02267	0.7367E-03
PVAc	0.02449	0.7150E-03
LDPE	0.00735	0.2047E-03

$$\Psi_{mn} = \exp\left(-\frac{a_{mn} + b_{mn}T + c_{mn}T^2}{T}\right), \tag{14}$$

where a_{mn}, b_{mn}, and c_{mn} are the interaction parameters.

As mentioned above, two different mixing rules were used to couple the equations of state with the UNIFAC G^E model: the universal mixing rule (UMR) proposed by Voutsas et al. (2004) and a universal and generic mixing ule (UGMR) presented in Staudt et al. (2009). An important aspect is that the above mentioned mixing rules do not rely on empirical binary interaction parameters originating powerful and total predictive tools.

The CEOS parameters a and b of the solvents are determined from Equation 2 and Equation 3, respectively, using its critical properties and acentric factor. For polymers, the a and b parameters depend on ρ^* and T^*, accordingly to Equation 7 and Equation 8, respectively.

The VLE data are taken from Hao (1991) for poly (methyl methacrylate) (PMMA), from Wohlfarth (1994) and Hao et al. (1991) for poly(styrene) (PS), poly (isobutylene) (PIB), poly (ethylene oxide) (PEO) and poly (vinyl acetate) (PVAc). For low-density polyethylene (LDPE), VLE data from Surana et al. (1997) and for poly (dimethyl siloxane) (PDMS), the data was taken from Hwang et al. (1998).

4. Pure Polymer Results

In this section, the volumetric behavior of pure polymer liquids over a wide range of temperature and pressure is analyzed.

In Figures 1, 2 and 3, the results of isobaric experiments for PIB, PS and poly(vinyl chloride) (PVC), are shown. SRK-W EOS results were not included when $|\Delta v\%| > 15\%$.

As can be seen above, the results of our proposal for pure polymer PVT behavior at low pressure are quite satisfying for a wide temperature range. Because of the $a(T)$ function obtained in this work, the molar volume prediction in isobaric experiments show lower errors and do not present the systematic error shown by PR-LT EOS. The deviations found in very high pressure tests ($>$ 300 bar) are slightly more significant than those found in figures above, however the predictions of the VLE of systems involving polymer-solvent mixtures at high pressures show good agreement with experimental data.

In Figures 4, 5 and 6, isothermal tests are presented.

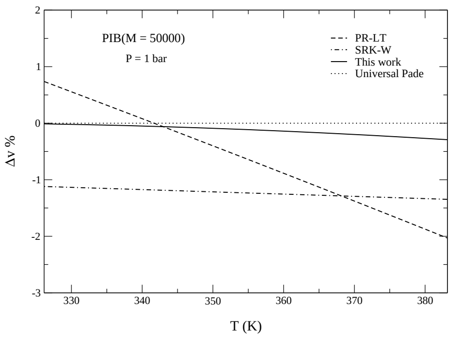

Figure 1: Percent error in molar volume of PIB(50000) at 1 bar.

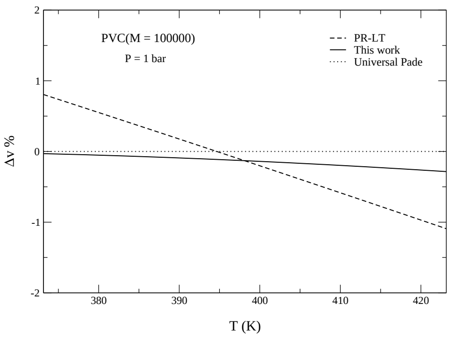

Figure 3: Percent error in molar volume of PVC(100000) at 1 bar.

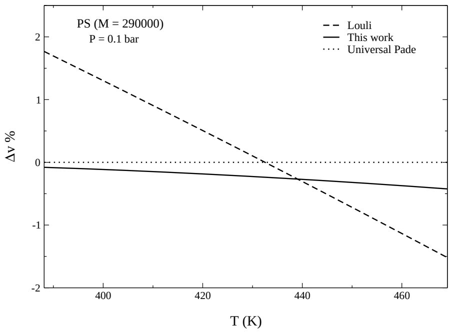

Figure 2: Percent error in molar volume of PS(290000) at 0.1 bar.

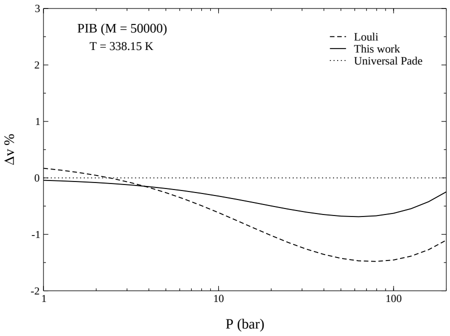

Figure 4: Percent error in molar volume of PIB(50000) at 338.15K.

Once more, the equation proposed show better results over a wide range of pressure. For PS, the PR-LT equation show better result at low pressure and almost the same answer as the pressure increases.

5. VLE of Polymer Solutions

Bubble point calculations were carried out for several polymer-solvent systems. A wide range of temperature, pressure and molecular weight was investigated. Results for systems containing PIB and PS can be seen in Figures 7 to 10.

For PIB and PS systems, all models tested showed good agreement with the experimental data. Some EOS's were excluded of some pictures in order to make the visualization easier. Just the best results were kept. The UGMR performed slightly better for the majority of the cases, specially with the CEOS developed in this work.

The results for the low density polyethylene (LDPE) with several solvents are illustrated in Figures 11 to 14.

In these systems, the SRK-W EOS showed bigger discrepancies from the experimental data. Again, the EOS proposed here and the PR-LT presented very similar results, even at high pressures (around 30 and 40 bar).

In Figures 15 to 18 another polymeric systems can be seen. For PMMA and PDMS no SRK-W parameters are available.

Once more, the equation proposed here and the PR-LT showed the best results, both combined with UGMR. Although our CEOS is based only on pure polymer liquid PVT data, the results polymer-solvent VLE are quite good when it is coupled with mixing rules from the literature. The proposed methodology has the advantage of having the parameters available for 61 differente polymers, contrasting with 19 and 9 available for PR-LT and SRK-W equations, respectively.

6. Conclusions

An alternative cubic equation of state was proposed. This equation is based on a temperature-pressure superposition principle developed to represent pure polymer liquid PVT data. Its applicability goes beyond pure systems, and very good results can be found for polymer-solvent VLE problems. The equation parameters a and b are calculated with characteristic temperature and mass density available for 61 different polymers. Among the main advantages of this alternative method, we can cite: a) the easy implementation in commercial softwares, once the equation is based on an generic form of CEOS like Peng Robinson and Soave Redlich Kwong ones; b) can be used to predict the behavior of pure polymer liquid or polymer solutions; c) has a temperature dependent attractive term $a(T)$, and d) does not involve binary interaction empirical parameters.

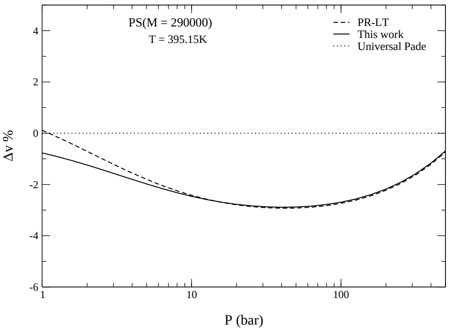

Figure 5: Percent error in molar volume of PS(290000) at 395.15K.

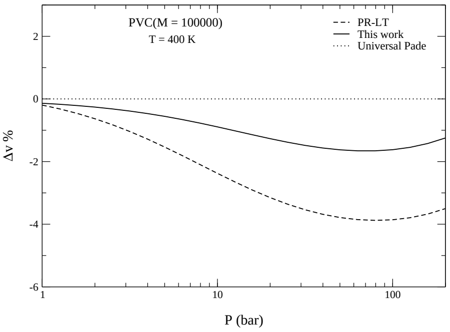

Figure 6: Percent error in molar volume of PVC(100000) at 400K.

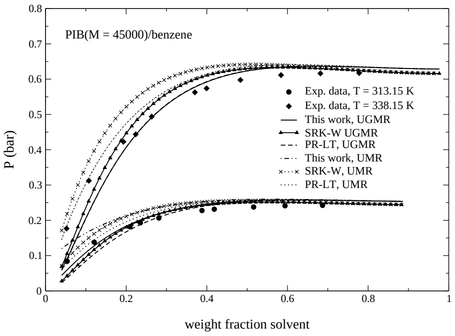

Figure 7: Results of bubble point pressure for systems containing PIB and benzene.

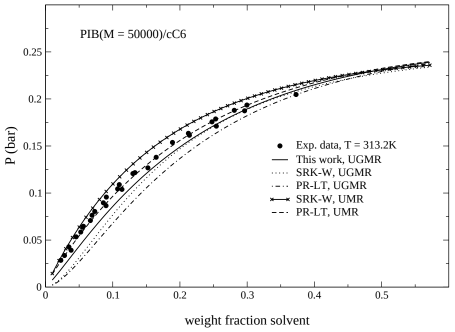

Figure 8: Results of bubble point pressure for systems containing PIB and cyclohexane.

The predicted pure liquid molar volume and bubble point for polymer-solvent systems were compared with PR-LT and SRK-W. These equations make use of a temperature independent attractive term assuming that a/M and b/M are independent of molecular weight M. Besides, two mixing rules were tested: the UMR and the UGMR combining the EOS with a UNIFAC model to evaluate the Gibbs free energy. The results with the equation proposed and UGMR are quite promising, showing the adequacy of the new method for predicting thermodynamic polymer behavior.

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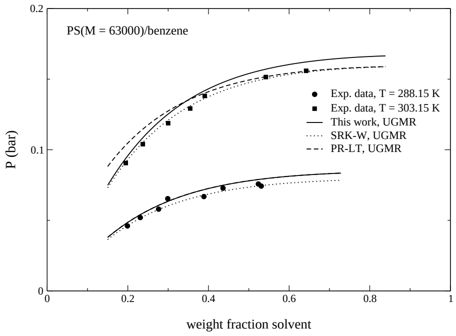

Figure 9: Results of bubble point pressure for systems containing PS and benzene.

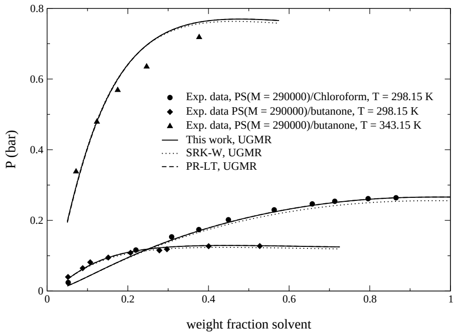

Figure 10: Results of bubble point pressure for systems PS and several solvents.

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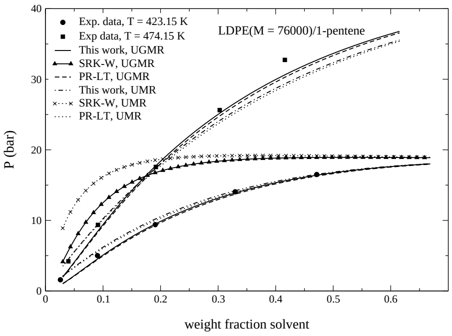

Figure 11: Results of bubble point pressure for systems containing LDPE and 1-pentene.

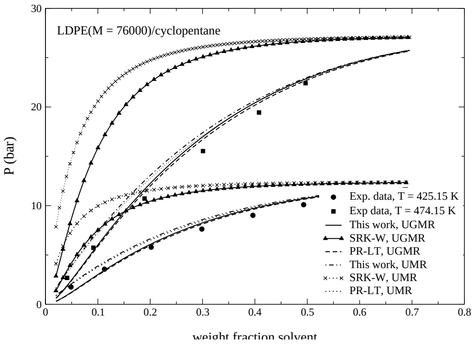

Figure 12: Results of bubble point pressure for systems containing LDPE and cyclopentane.

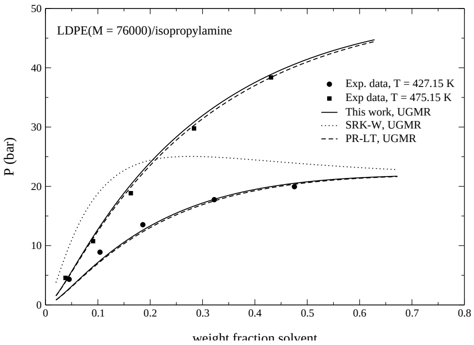

Figure 13: Results of bubble point pressure for systems containing LDPE and isopropylamine.

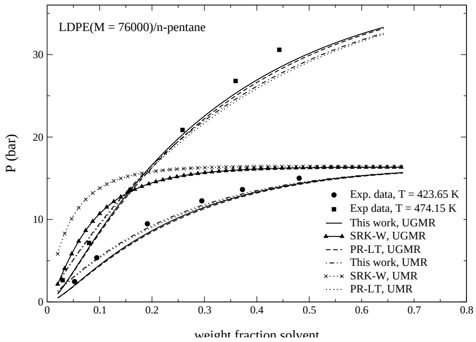

Figure 14: Results of bubble point pressure for systems containing LDPE and n-pentane.

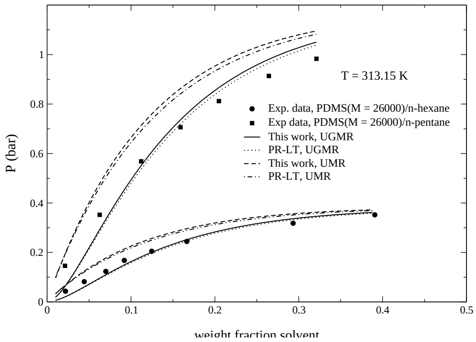

Figure 15: Results of bubble point pressure for systems containing PDMS.

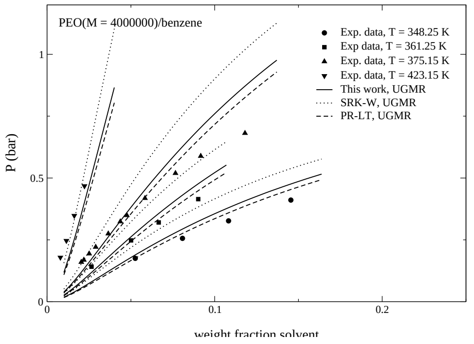

Figure 16: Results of bubble point pressure for systems containing PEO.

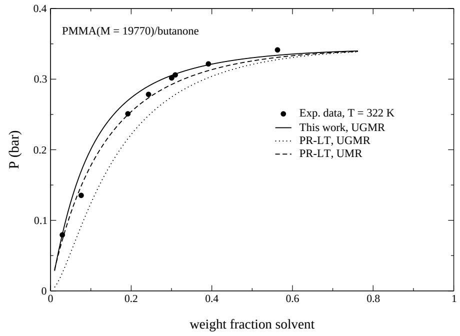

Figure 17: Results of bubble point pressure for systems containing PMMA.

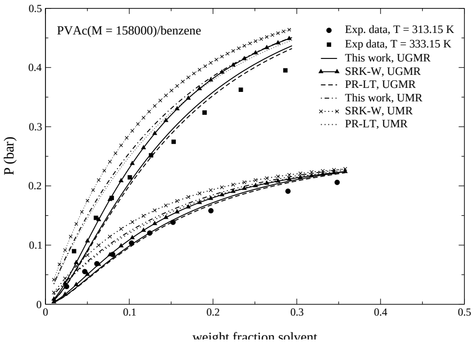

Figure 18: Results of bubble point pressure for systems containing PVAc.