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A new cubic equation of state for prediction of VLE of polymer solutions

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ABSTRACT

A new 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 results are 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 showed 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.

1. Introduction

Cubic equations of state (CEOS) are widely used in engineering for computing phase equilibrium and thermodynamic properties of simple mixtures. Most of the CEOS available today are special cases of a generic cubic equation [1], 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.

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.

Besides the predictive potential of CEOS, three additional aspects have been determining for the interest in extending the use of this type of EOS for polymers and other complex systems: (i) numeric and analytical procedures for dealing with a great variety of properties calculation and phase equilibrium problems are well established for CEOS; (ii) implementations of CEOS are available in most commercial computational packages for thermodynamic applications; (iii) 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 [2–8].

One of the most relevant aspects when dealing with the application of CEOS for polymeric systems is the calculation of $a(T)$ and b. For most 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 they degrade before reaching the critical point. To overcome this difficulty, it usual to predict the critical parameters and acentric factor using group contribution methods like Constantinou and Gani [9], Joback and Reid [10], and so on. Through this methodology the calculation is straightforward, but the group parameters used are strongly dependent on the specific structural features of the molecules and are common for closely related compounds only. Another alternative is the direct estimation of the $a(T)$ and b terms

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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	$\alpha_{SRK}(T_r;\omega)$ [a]	1	0	0.08664	0.42748
PR	$\alpha_{PR}(T_r;\omega)$ [b]	$1+\sqrt{2}$	$1-\sqrt{2}$	0.07780	0.45724

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

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

using pressure–volume–temperature (PVT) and vapor–liquid equilibrium (VLE) data [6,8,11,12]. Although the results with fitted a and b parameters are quite accurate, their range of applicability is limited to the experimental domain.

Several works in literature use CEOS to estimate pure polymer properties and the phase equilibrium of polymer solutions [6,8,11–13]. In general, the results are reasonable, but most of times the use of empirical binary interaction parameters or other experimental adjustments is mandatory. The main disadvantage of using empirical binary interaction parameters is their system and temperature dependence, which significantly narrows the range of reliability of the predictions.

Sako et al. [14] 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. Orbey and Sandler [12], using a different approach, 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. [13] used a polymer SRK equation to correlate polyethylene–ethylene mixtures and compared the results with the Sanchez–Lacombe and SAFT calculations. They showed that each equation of state has some unique characteristics that affect the outcome of modeling pure component as well as mixture behavior. Kalospiros and Tassios [15] found satisfactory results with the use of a simplified Wong–Sandler mixing rule proposed by Zhong and Masuoka [6] for alkane/alkane mixtures, alkane/polymer mixtures and polymer/solvent mixtures.

Recently, Louli and Tassios [11] proposed a new cubic equation based on the Peng–Robinson EOS with an interesting 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 [8] 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.

Almeida et al. [16] applied the mixing rule of Zhong and Masuoka [6] with pure polymer parameters from Louli and Tassios [11]. The system studied was the phase equilibrium of a mixture composed by styrene, ethyl-benzene and polystyrene in a polymerization reactor. The results showed a good agreement with data from an industrial reactor but the model presented a significant sensitivity to the binary interaction parameters.

Taking into account the aspects discussed above, this work presents a new CEOS in which the usual relations for $a(T)$ and b based on critical properties are replaced by an approximation derived from the temperature–pressure superposition principle [17–19]. Additionally, the use of this CEOS combined with excess Gibbs free energy (G^E) mixing rules, which do not rely on empirical binary interaction parameters, is proposed as a methodology to the analysis of phase equilibrium for complex mixtures involving polymers. This methodology is expected to present the following features:

- easiness of implementation in computational thermodynamic packages;
- high accuracy in the prediction of the behavior of pure polymer liquids and polymer solutions.

In Section 2 the new equation is proposed and the mixing rules used to extend its applicability to polymer solutions are presented. In Section 3 the predictions obtained with the proposed equation for pure polymer liquid behavior and phase equilibrium in polymer solutions are compared with literature data and other EOS's, attesting the appropriate form of the new model.

2. Methodology

2.1. A new CEOS for pure polymers and polymer solutions

Sanchez and Cho [17] proposed a semi-empirical equation of state to describe pure polymer liquids behavior. This equation was based on the temperature–pressure superposition principle and on the empirical observation that for polymer liquids both density and the logarithm of the bulk modulus are linear functions of temperature. This equation gives predictions of PVT behavior for pure polymer liquids with accuracy comparable to experimental data [17] and uses a single set of three parameters to represent the polymer: the characteristic temperature T^*, pressure P^* and mass density ρ^*. The characteristic parameters of Sanchez and Cho [17] are not properties that can be directly measured, as the critical properties, for instance. But the authors suggested that the characteristic parameter ρ^* is inversely proportional to the van der Waals volume. In spite of its great performance and accuracy to determine pure compound properties, this equation cannot be used to predict polymer behavior in solution and consequently it is not applicable in polymerization reactions simulation, membrane synthesis, and so on.

Taking advantage of the simplicity of CEOS and the great accuracy of the equation proposed by Sanchez and Cho [17], a new CEOS attractive term $a(T)$ is proposed as follow.

Using the simple relation for the reduced density $\tilde{\rho}_0 \equiv \rho_0/\rho^*$, derived from the aforementioned principle in Sanchez and Cho [17], we can write:

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

where $\tilde{T} \equiv T/T^*$ and ρ_0 is the mass density at T and reference pressure P_0. Using Eq. (4), we obtain the molar volume at P_0:

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

From the generic form of the CEOS (Eq. (1)), we can isolate the $a(T)$ term:

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

For low pressures, that is $P = P_0 \approx 0$ and as a consequence $v = v_0$, we can simplify Eq. (6) and define a new form for $a(T)$ to be used in CEOS's:

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

where v_0 is only a function of temperature as stated in Eq. (5). Additionally, the co-volume parameter b is chosen as a function of the