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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.

Keywords: Copolymer; Vapor–liquid equilibrium; Equation of state

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 worldwide 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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Abbreviations: ACE, acetone; BTD, butadiene; BZN, benzene; CHL, chloroform; ET, ethylene; nC_4OH, 1-butanol; nC_5, *n*-pentane; nC_6, *n*-hexane; cC_6, cyclohexane; PB, poly(butadiene); PE, high-density poly(ethylene); PS, poly(styrene); PSBR, poly(styrene-*co*-butadiene); PVA, poly(vinyl acetate); PVAE, poly(vinyl acetate-*co*-ethylene); PVAVC, poly(vinyl acetate-*co*-vinyl chloride); PVC, poly(vinyl chloride); STR, styrene; VA, vinyl acetate; VC, vinyl chloride; TOL, toluene

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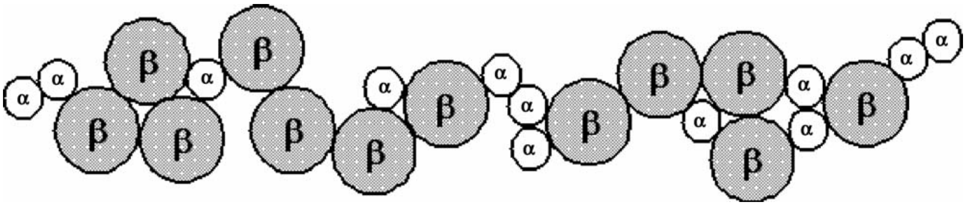

Fig. 1. Molecular model for a copolymer of type poly(α-*co*-β), containing monomers α and β.

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:

$$Z = \tilde{v} r \ln\left[\frac{\tilde{v}}{\tilde{v}-1}\right] + \frac{Z_C}{2}\tilde{v} r \ln\left[\frac{\tilde{v}-1+(q/r)}{\tilde{v}}\right] + l - \frac{\tilde{v}\Psi(q/r)}{\tilde{v}-1+(q/r)}\sum_{i=1}^{n_c}\sum_{a=1}^{n_g} x_i \nu_i^a Q^a \frac{\Gamma^a - 1}{\tilde{v}-1+(q/r)\Gamma^a} \quad (1)$$

where Z is the compressibility factor, ν_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:

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

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

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

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

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

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:

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

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

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

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

$$\ln \hat{\phi}_i = -r_i \ln\left[\frac{\tilde{v}-1}{\tilde{v}-1+(q/r)}\right] + (1-l_i)\ln\left[\frac{\tilde{v}}{\tilde{v}-1+(q/r)}\right] + \frac{\Psi(q/r)(q_i - r_i)}{\tilde{v}-1+(q/r)} + \Psi\sum_{a=1}^{n_g}\nu_i^a Q^a \ln\left[\frac{\tilde{v}-1+(q/r)}{\tilde{v}-1+(q/r)\Gamma^a}\right] - \frac{\Psi}{r}\sum_{k=1}^{n_c}\sum_{a=1}^{n_g} x_k \nu_k^a Q^a \frac{\sum_{e=1}^{n_g}\nu_i^e Q^e \gamma^{ea} - r_i}{\tilde{v}-1+(q/r)\Gamma^a} - \ln Z \quad (10)$$