

## Application of Cubic Equation of State Models in Prediction of Vapor–Liquid Equilibria for Binary Polyvinyl Acetate/Solvent Solutions

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**ABSTRACT:** The cubic equation of state (CEoS) is a powerful method for calculation of (vapor + liquid) equilibrium (VLE) in polymer solutions. Using CEoS for both the vapor and liquid phases allows one to calculate the non-ideality of polymer solutions based on a single EoS approach. In this research, vapor–liquid equilibria calculations of polyvinyl acetate (PVAc)/solvent solutions were performed. In this approach, eight models containing PRSV and SRK CEoS separately combined with four mixing rules namely vdW1, vdW2, Wong–Sandler (WS), and Zhong–Masuoka (ZM) were applied to calculations of bubble point pressure. For the better prediction, the adjustable binary interaction parameters existing in any mixing rule were optimized. The results were very acceptable and satisfactory. Absolute average deviations (%AAD) between predicted results and experimental bubble point pressure data were calculated and presented. The capability of two cubic equations of state had a good agreement with experimental data and predict the correct type of phase behavior in all cases, but the performance of the PRSV + vdW2 was more reliable than the other models with 2.65% in AAD for total of solution systems. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40651.

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### INTRODUCTION

Thermodynamics of polymers have possessed much attention during the last decades and modeling of the phase equilibrium of polymeric systems is becoming increasingly principal for a numerous industrial processes and products.<sup>1</sup>

Polyvinyl acetate (PVAc) is a thermoplastic polymer with the formula  $(C_4H_6O_2)_n$ , obtained by polymerization of vinyl acetate using a suitable initiator, without solvent or with water or 2-propanol (free radical vinyl polymerization of the monomer vinyl acetate).<sup>2</sup> The index  $n$  is about 100–17,000. The relative molecular mass lies between 10,000 and 15,000,000.<sup>3</sup>

The applications of PVAc in industrial fields are realized as additives for antishrink, antifatigue in glass fiber reinforced concrete industry, antiwarping, adhesives, color enhancing, strength enhancing, etc. Meanwhile, PVAc is also largely required in food and medical industries like gumbase and medicals. Gumbase industry for chewing gum, bubble gum, and xylitol, etc. In medicals, PVAc is applicable because it is green and eco-friendly product.<sup>4</sup>

The knowledge of the phase behavior of polymer solutions are of extreme importance for the development of several polymer processes, such as the recovery and separation of organic vapors using polymeric membranes, the production of paints and coatings,<sup>5,6</sup> the impregnation of polymers, the encapsulation of pharmaceutical substances in biodegradable polymer matrices,<sup>7</sup> and the production of polymer nano composites and films using solution casting methods.<sup>8,9</sup> Furthermore, the phase behavior of polymer–solvent systems is momentous in polymer synthesis, because many polymeric products are produced with a solvent (or a mixture of solvents) and often other low molecular weight compounds (plasticizers, etc.). Consequently, a problem which often arises is how to eliminate the residual solvents and low molecular weight constituent(s) from the final product (polymer). In particular, the removal of solvents is important for polymeric materials used in the food and pharmaceutical industry.<sup>10</sup> The solution to this problem involves, among other tasks, solving the vapor–liquid equilibrium 2 (VLE) problem in which the solvent activity needs to be known (in conditions often close to infinite dilution).<sup>11</sup>

This article was published online on 19 March 2014. An error was subsequently identified. This notice is included in the online and print versions to indicate that both have been corrected 21 April 2014.

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**Table I.** Specific Cubic Equation Parameters

EOS	$\alpha(T_r)$	$\sigma$	$\varepsilon$	$\Omega$	$\Psi$
vdW	1	0	0	1/8	27/64
RK	$T_r^{-1/2}$	1	0	0.08664	0.42748
SRK	$\alpha_{\text{SRK}}(T_r; \omega)^a$	1	0	0.08664	0.42748
PR	$\alpha_{\text{PR}}(T_r; \omega)^b$	$1 + \sqrt{2}$	$1 - \sqrt{2}$	0.07780	0.45724

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

$$^b \alpha_{\text{PR}}(T_r; \omega) = [1 + (0.37464 + 1.5422\omega - 0.26992\omega^2)(1 - T_r^{1/2})]^2$$

In the last few years, there has been an increase in publications on the VLE for polymer/solvent systems.<sup>1,6,12–14</sup> However, development of accurate thermodynamic models for polymer solutions is also vital in the design of advanced polymeric materials and separation process that use polymer solutions.

The available thermodynamic models for the prediction of the polymer solution properties can be classified into two main categories: the lattice base and the van der Waals base models. Some models have offered based on the van der Waals theory while several authors<sup>15–18</sup> further developed the models according to the lattice base. These bases have been applied for the expansion of various activity coefficient models as well as equations of state.<sup>12</sup> Then, modeling of the polymer solution needs an accurate equation of state to predict the phase equilibrium of such systems with appropriate mixing rules.

Cubic equations of state (CEoS) are extensively applied in engineering for computing phase equilibrium and thermodynamic properties of simple mixtures. 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 calculation of a vast 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.<sup>19–22</sup>

The objective of this work is predicting of vapor–liquid equilibria of PVAc/solvent solutions by PRSV and SRK cubic equations of state using four mixing rules namely: Van der Waals one-fluid mixing rule with one adjustable parameter (vdW1), Van der Waals one-fluid mixing rule with two adjustable parameters (vdW2), Wong–Sandler (WS) combining with Flory–Huggins (FH) activity coefficient model and Zhong–Masuoka (ZM) mixing rule separately. Later, investigation of validity and accuracy of these models was performed and compared. Finally, the obtained results of absolute average deviations (%AAD) between predicted

results and experimental bubble point pressure data in each model were compared with achieve the best.

## THERMODYNAMIC MODEL

### VLE Calculation for Polymer Solutions

For the VLE calculations on mixtures, the equal fugacity criterion is used for each component  $i$ :

$$\hat{f}_i^V = \hat{f}_i^L, \quad i = 1, 2, \dots, N \quad (1)$$

For polymer solutions, the quantity of polymer in the vapor phase is close to zero. It is convenient to assume that there is no polymer in the vapor phase and eq. (1) is only applied for the solvent molecule.

The phase equilibria equation for solvent in a polymer solution can be expressed as:

$$\varphi_1^V P = x_1 \varphi_1^L P \quad (2)$$

where  $\varphi_1^L$  and  $\varphi_1^V$  are the fugacity coefficients of solvent in the liquid and vapor phases, respectively. It should be noted that the vapor phase is only pure solvent and vaporization of polymer may be ignored. So, the fugacity coefficient<sup>23</sup> can be obtained in both phases as:

$$RT \ln \varphi_i^V = \int_{V^V}^{\infty} \left[ \left( \frac{\partial P}{\partial n_i} \right)_{T, V, n_{j \neq i}} - \frac{RT}{V} \right] dV - RT \ln Z_{\text{mix}}^V \quad (3)$$

$$RT \ln \varphi_i^L = \int_{V^L}^{\infty} \left[ \left( \frac{\partial P}{\partial n_i} \right)_{T, V, n_{j \neq i}} - \frac{RT}{V} \right] dV - RT \ln Z_{\text{mix}}^L \quad (4)$$

where  $Z_{\text{mix}}$  is the compressibility factor of the vapor or liquid mixture.

### Cubic Equations of State

Most of the CEoS available today are special cases of a generic cubic equation,<sup>24</sup> which can be written as:

$$P = \frac{RT}{V-b} - \frac{a(T)}{(V+\varepsilon b)(V+\sigma b)} \quad (5)$$

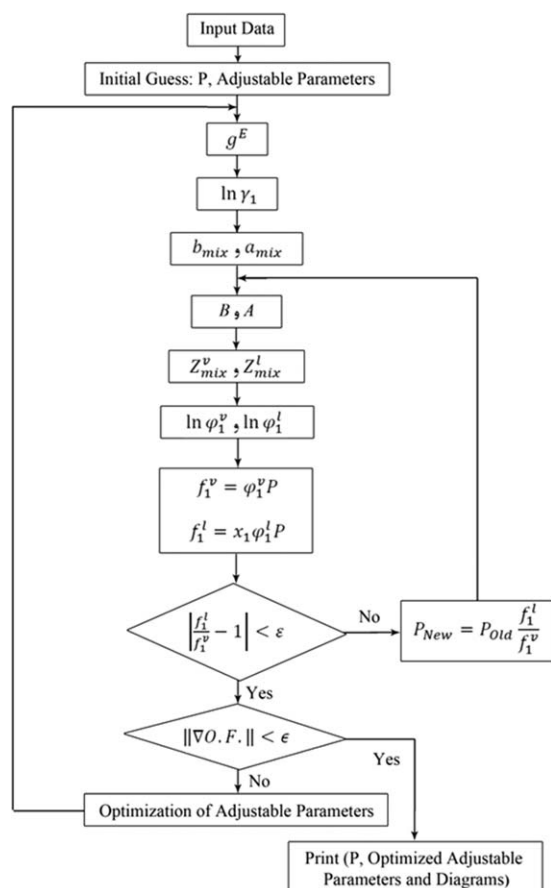
where  $\varepsilon$  and  $\sigma$  are constants for all substances and depend on the EoS (Table I) and  $a(T)$  and  $b$  are, respectively, the attractive

**Table II.** CEoS Parameters for PVAc Calculated with Louli and Tassios<sup>13</sup>

Polymer	$T$ range (K)	$P$ range (bar)	$a/MW$	$b/MW$	AAE% in V
PVAc	308.15–373.15	0–800	1,847,343	0.8428	1.38

$a$  ( $\text{cm}^6 \text{ bar/mol}^2$ ) and  $b$  ( $\text{cm}^3/\text{mol}$ ).

AAE% =  $\Sigma \text{abs}(V_{\text{cal}} - V_{\text{exp}})/V_{\text{exp}}/NP \times 100$ .



**Figure 1.** Computational algorithm based on bubble point pressure calculations for binary polymer solutions.

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:

$$a(T) = \psi \frac{\alpha(T_r, \omega) R^2 T_c^2}{P_c} \quad (6)$$

$$b = \Omega \frac{RT_c}{P_c} \quad (7)$$

where  $T_c$  is the critical temperature,  $P_c$  is the critical pressure,  $\omega$  is the acentric factor,  $T_r = T/T_c$  the reduced temperature and the other symbols are shown in Table I. As can be seen in Table I, the specific values of  $\Omega$ ,  $\sigma$ , 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 polymers, the critical point is not measurable; this means that the CEoS parameters  $a$  and  $b$  cannot be calculated from the critical data. In this work, the polymer parameter  $a$  and  $b$  are evaluated based on literature that are no longer temperature-dependent.<sup>13</sup> In calculations, where the polymer's molecular weight differs from those of the reference paper,<sup>13</sup> the parameters  $a$  and  $b$  of a specified polymer were calculated by assuming the  $a/MW$  and  $b/MW$  parameters are identical for the polymer with different molecular weight, i.e.,  $a/MW$  and  $b/MW$  are characteristic for the type of polymer but independent of

polymer structure (chain length or molecular weight distribution). Table II lists the parameter  $a/MW$  and  $b/MW$  for the CEoS of the PVAc.

**PRSV EoS.** A modification to the attraction term in the Peng–Robinson equation of state published by Stryjek and Vera in 1986 (PRSV) significantly improved the model's accuracy by introducing an adjustable pure component parameter and by modifying the polynomial fit of the acentric factor.<sup>25</sup>

In this work, PRSV EoS is used as:

$$P = \frac{RT}{v-b} - \frac{a}{v^2 + 2vb - b^2} \quad (8)$$

$$a = 0.457235 \frac{R^2 T_c^2}{P_c} \alpha \quad (9)$$

$$b = 0.077796 \frac{RT_c}{P_c} \quad (10)$$

$$\alpha = [1 + k(1 - T_r^{0.5})]^2 \quad (11)$$

The modification is:

$$k = k_0 + k_1(1 + T_r^{0.5})(0.7 - T_r) \quad (12)$$

$$k_0 = 0.378893 + 1.4897153\omega - 0.17131848\omega^2 + 0.0196554\omega^3 \quad (13)$$

$$T_r = \frac{T}{T_c} \quad (14)$$

where  $k_1$ ,  $\omega$  are adjustable pure component parameter and acentric factor of the species, respectively. Stryjek and Vera reported pure component parameters for many compounds of industrial interest.

For estimation of  $Z_{\text{mix}}$ , the PRSV EoS can be written as follows:

$$Z_{\text{mix}}^3 - (1-B)Z_{\text{mix}}^2 + (A-3B^2-2B)Z_{\text{mix}} - (AB-B^2-B^3) = 0 \quad (15)$$

$$A = \frac{a_{\text{mix}} P}{R^2 T^2} \quad (16)$$

$$B = \frac{b_{\text{mix}} P}{RT} \quad (17)$$

The  $a_{\text{mix}}$  and  $b_{\text{mix}}$  are the mixture parameters of CEoS that were calculated using different mixing rules.

**SRK EoS.** In this work, SRK EoS<sup>26</sup> is used as:

$$P = \frac{RT}{v} - \frac{a}{v(v+b)} \quad (18)$$

$$a = 0.42747 \frac{R^2 T_c^2}{P_c} \alpha \quad (19)$$

$$b = 0.08664 \frac{RT_c}{P_c} \quad (20)$$

$$\alpha = [1 + (0.48508 + 1.55171\omega - 0.15613\omega^2)(1 - T_r^{0.5})]^2 \quad (21)$$

For estimation of  $Z_{\text{mix}}$ , the PRSV EoS can be written as follows:

$$Z_{\text{mix}}^3 - Z_{\text{mix}}^2 + (A-B-B^2)Z_{\text{mix}} - AB = 0 \quad (22)$$

### Mixing Rules

The ability of a CEoS to correlate and predict phase equilibria of mixtures depends strongly on the mixing rule applied. Among several mixing rules suggested, the following are the most popular and adopted methods were chosen to test the

**Table III.** Calculated Results of Absolute Average Deviations (%AAD) Between Predicted and Experimental Bubble Point Pressure Data for PVAc/Solvent Solutions with Various Models Containing PRSV and SRK CEOS Combining with Different Mixing Rules

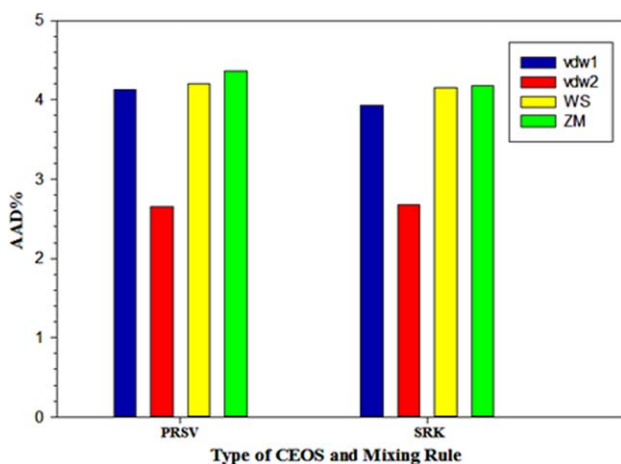
No.	System	Ref.	T (K)	MW (g/mol)	NP	AAD (%)							
						PRSV				SRK			
						Vdw1	Vdw2	WS	ZM	Vdw1	Vdw2	WS	ZM
1	PVAc+benzene	14	313.15	158000	10	3.2	1.7	7.5	2.6	2.8	2.2	7.6	2.6
2	PVAc+benzene	14	333.15	158000	9	3.4	1.1	2.9	1.9	2.8	1.1	3.1	1.9
3	PVAc+methanol	1	313.2	167000	11	4	3.8	7.5	7.8	4.5	3.8	7.5	7.6
4	PVAc+methanol PVAc+methanol	1	333.2	167000	9	3.5	1.6	2.7	3.8	2.8	1.6	2.6	3.2
5	PVAc+acetone	1	353.2	167000	9	5.4	0.9	2.7	3.1	4.7	0.9	2.5	3
6	PVAc+acetone	1	313.2	167000	8	5.9	2.2	3.2	7.6	6.5	2.2	3.3	7.5
7	PVAc+acetone	1	333.2	167000	7	0.6	0.6	1	1.2	0.7	0.6	0.9	1
8	PVAc+propylamine	1	353.2	167000	5	3.6	3.4	4.1	4.3	3.8	3.4	4.1	4
9	PVAc+2-propanol	1	313.2	100000	4	2.3	2.1	5.2	2	2.2	2.1	5.6	2.1
10	PVAc+2-propanol	1	313.2	167000	10	9.8	8.5	5.2	5.9	9.3	8.3	5.2	5.9
11	PVAc+2-propanol	1	333.2	167000	10	1.8	1.5	3.1	3.9	1.5	1.5	2.7	3.5
12	PVAc+chloroform	1	353.2	167000	8	2.4	2.3	3.9	4.2	2.3	2.3	3.5	3.8
13		13	333.15	194000	7	5.6	3.8	4.8	6.1	5.6	3.8	4.1	5.9
Overall deviation					107	4.1	2.657	4.1998	4.36	3.928	2.673	4.1537	4.183

$AAD\% = \frac{AP}{P} \% = 100 \times \sum_{i=1}^{NP} \frac{|p^{calc} - p^{exp}|}{NP}$ ; NP, number of data points.

ability of the EoS to predict of phase equilibria behavior in polymer solutions.

**Vdw1 Mixing Rule.** The most commonly used method to extend equations of state to a non-polar mixture is to use the van der Waals one-fluid mixing rules.<sup>27</sup> This rule is capable of accurately representing vapor-liquid equilibria using only one binary-interaction parameter for non-polar or slightly polar systems.

$$a = \sum \sum x_i x_j a_{ij}, \quad (23)$$

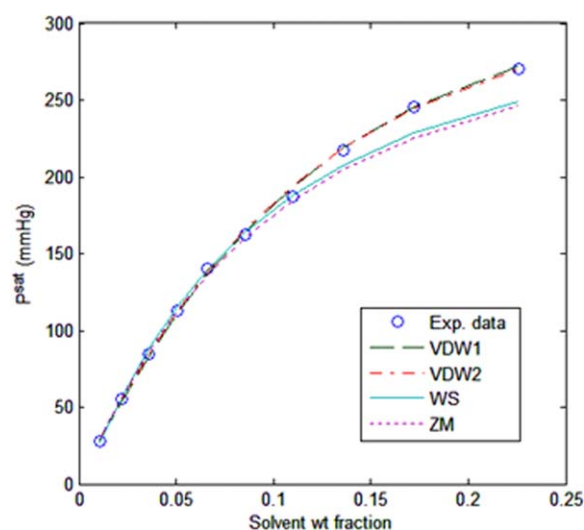


**Figure 2.** Overall result of absolute average deviations between models predicted and experimental of PVAc/solvent solutions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

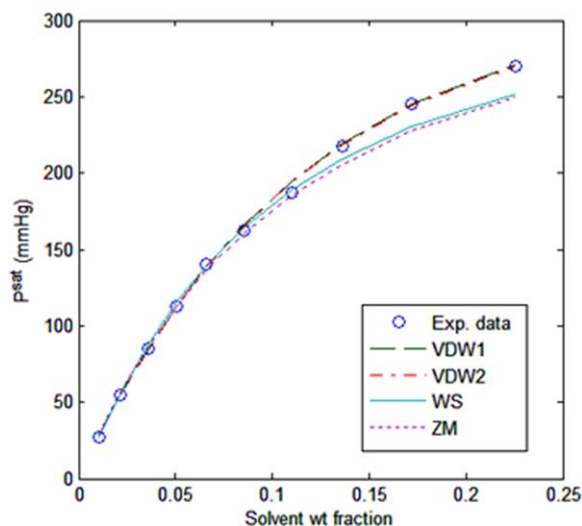
$$b = \sum x_i b_i, \quad (24)$$

$$a_{ij} = \sqrt{a_i a_j} (1 - k_{ij}) \quad (25)$$

where  $x_{i(j)}$ ,  $a_{ij}$  and  $k_{ij}$  are mole fraction, cross energy parameter, and binary interaction parameter, respectively. It is noted that  $k_{ij}$  can be obtained from the regression of VLE data.



**Figure 3.** Prediction of the bubble point pressure for systems containing PVAc ( $MW = 1,67,000$ ) + 2-Propanol at ( $T = 333.2$  K) with PRSV EOS models. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**Figure 4.** Prediction of the bubble point pressure for systems containing PVAc ( $MW = 1,67,000$ ) + 2-Propanol at ( $T = 333.2$  K) with SRK EOS models. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**Vdw2 Mixing Rule.** The second mixing rule is the conventional two-parameter van der Waals one-fluid mixing rule (vdW2):<sup>27</sup>

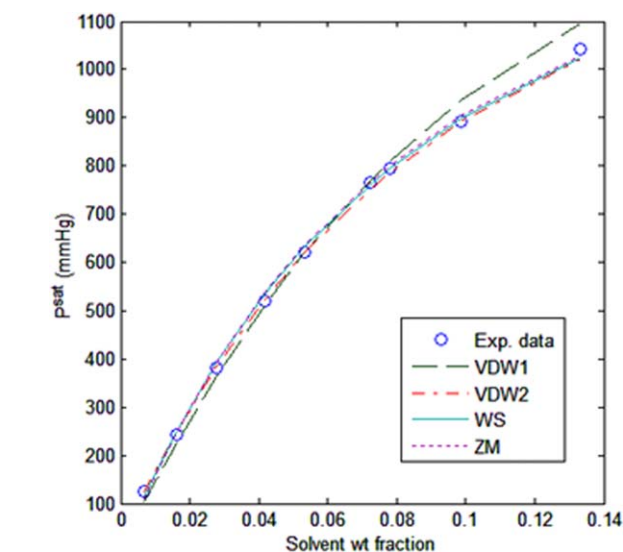
$$a = \sum_i \sum_j x_i x_j a_{ij}, \quad (26)$$

$$b = \sum_i \sum_j x_i x_j b_{ij}, \quad (27)$$

$$a_{ij} = \sqrt{a_i a_j} (1 - k_{ij}), \quad (28)$$

$$b_{ij} = \frac{b_i + b_j}{2} (1 - l_{ij}) \quad (29)$$

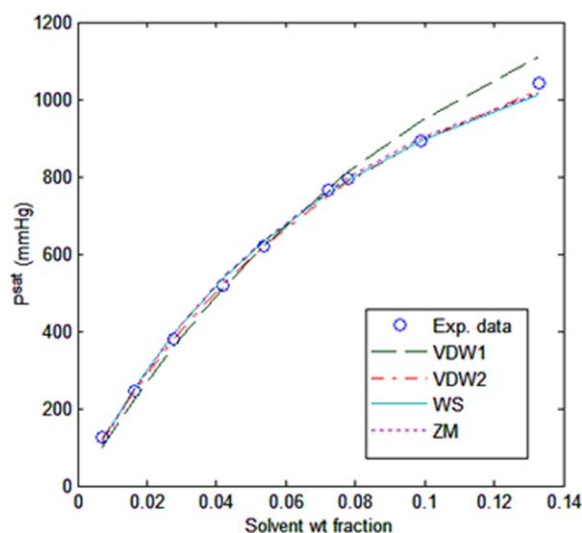
In these equations,  $a_{ij}$  and  $b_{ij}$  ( $i = j$ ) are parameters corresponding to pure component ( $i$ ) while  $a_{ij}$  and  $b_{ij}$  ( $i \neq j$ ) are called the unlike-interaction parameters. The binary interaction parameter



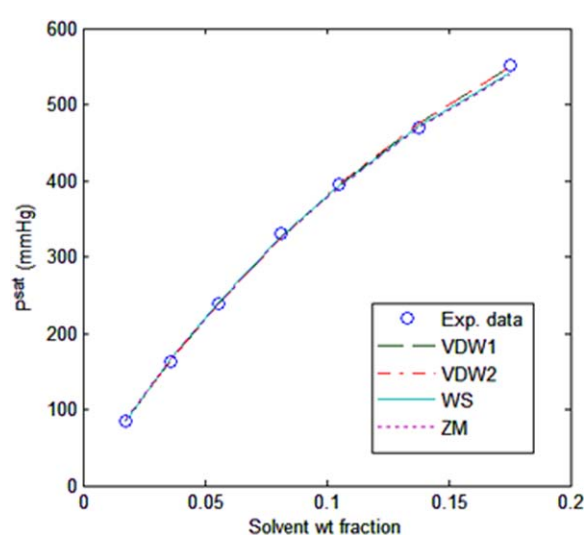
**Figure 6.** Correlation of saturation pressure for systems containing PVAc ( $MW = 1,67,000$ ) + Methanol at ( $T = 353.2$  K) with SRK EOS models. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

$l_{ij}$  can also be obtained from the regression of VLE data just as obtained for  $k_{ij}$ .

**Wong–Sandler Mixing Rule.** This mixing rule has been used extensively for correlating vapor–liquid equilibrium.<sup>28</sup> In this approach,  $a$  and  $b$  parameters in a mixture are determined in such a way that while the low-density quadratic composition dependence of the second virial coefficient is satisfied, the excess Helmholtz energy at infinite pressure from the equation of state is also equal to that of an appropriately chosen liquid activity coefficient model. The mixing rule for a two-parameter cubic equation is:

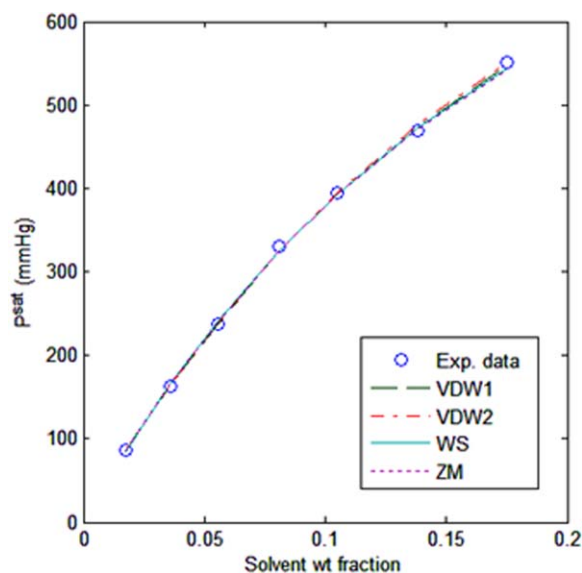


**Figure 5.** Correlation of bubble point pressure for systems containing PVAc ( $MW = 1,67,000$ ) + Methanol at ( $T = 353.2$  K) with PRSV EOS models. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 7.** VLE diagram for systems containing PVAc ( $MW = 1,67,000$ ) + Acetone at ( $T = 333.2$  K) with PRSV EOS models. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]





**Figure 8.** VLE diagram for systems containing PVAc ( $MW=1,67,000$ ) + Acetone at ( $T=333.2$  K) with SRK EOS models. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

$$b_m = \frac{Q}{1-DD}, \quad (30)$$

$$\frac{a_m}{RT} = Q \frac{DD}{1-DD}, \quad (31)$$

$$Q = \sum_i \sum_j x_i x_j \left( b - \frac{a}{RT} \right)_{ij}, \quad (32)$$

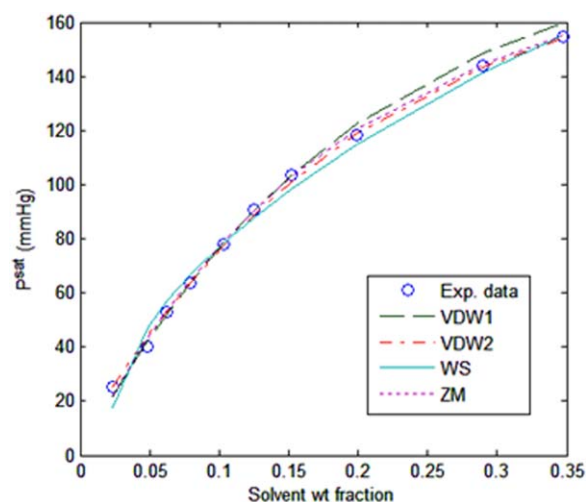
$$\left( b - \frac{a}{RT} \right)_{ij} = \frac{1}{2} \left[ \left( b_i - \frac{a_i}{RT} \right) + \left( b_j - \frac{a_j}{RT} \right) \right] (1 - k_{ij}) \quad (33)$$

$$DD = \sum x_i \frac{a_i}{b_i RT} + \frac{A_\infty^E}{CRT}, \quad (34)$$

where  $C$  is a constant equal to  $(1/\sqrt{2})\ln(\sqrt{2}-1)$  and  $A_\infty^E$  is any suitable molar excess Helmholtz energy model at infinite pressure or equivalently an excess Gibbs energy model at low pressure. This has the advantage of incorporating excess energy models into equations of state in a theoretically correct way, and it can be used for the very accurate correlation and or prediction of VLE for highly non-ideal mixtures. For this work, the Flory–Huggins model has been chosen, which includes two contributions to the thermodynamics of binary polymer solutions, entropy of a thermal mixing due to size difference between the species, and an enthalpy of mixing due to difference of the intermolecular forces, as

$$\frac{A^E}{RT} = x_1 \ln \frac{\Phi_1}{x_1} + x_2 \ln \frac{\Phi_2}{x_2} + \chi \Phi_1 \Phi_2 (x_1 + x_2 r) \quad (35)$$

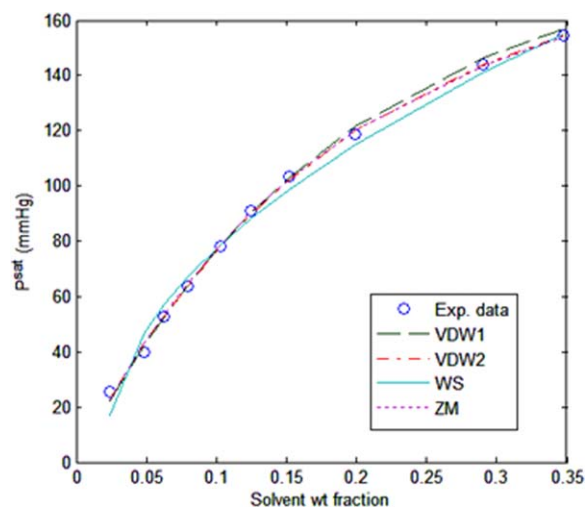
Herein,  $\chi$  is the Flory interaction parameter,  $\Phi$  is the volume fraction, and  $r$  is the number of solvent size segments that make up the polymer, which is approximated by the hardcore volumes. As the Flory–Huggins model is developed using a rigid, incompressible lattice, a PVT equation of state cannot be derived from it. However, the Wong–Sandler mixing rule provides a way of combining the Flory–Huggins model with an equation of state when the Helmholtz energies from the EoS



**Figure 9.** Comparison of the calculated results of bubble point pressure with experimental data for systems containing PVAc ( $MW=1,58,000$ ) + Benzene at ( $T=313.15$  K) with PRSV EOS models. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

and Flory–Huggins theory are equated at infinite pressure (the volume terms are replaced by the hard-core volume  $b$ ). With the selection of the PRSV CEoS and Wong–Sandler mixing rule, the fugacity coefficient of a species  $i$  in a homogeneous binary mixture is given in the Appendix.

**Zhong and Masuoka Mixing Rule.** Zhong and Masuoka<sup>21</sup> came up with a new mixing rule for extending cubic EoS to polymer solutions, refining the work done by Wong–Sandler.<sup>28</sup> Actually, the only difference between this mixing rule and the Wong–Sandler one is the absence of excess Helmholtz energy at infinite pressure,  $A_\infty^E$ , which was set equal to zero in this case.



**Figure 10.** Comparison of the calculated results of bubble point pressure with experimental data for systems containing PVAc ( $MW=1,58,000$ ) + Benzene at ( $T=313.15$  K) with SRK EOS models. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**Table IV.** Optimized Adjustable Binary Interaction Parameters Existing in Mixing Rules Used in this Article for PRSV CEOS

System	T (K)	MW	$(K_{ij})_{vdW1}$	$(K_{ij})_{vdW2}$	$(K_{ij})_{WS}$	$(K_{ij})_{ZM}$	$(l_{ij})_{vdW2}$	$r$	$\chi$
PVAc+benzene	313.15	1,58,000	0.611	0.815	0.996	0.910	0.581	5.00 E +03	1
PVAc+benzene	333.15	1,58,000	0.619	0.751	0.995	0.913	0.392	5.13 E +03	1
PVAc+methanol	313.2	1,67,000	0.632	0.593	0.995	0.955	-0.116	3.99 E +03	1
PVAc+methanol	333.2	1,67,000	0.640	0.730	0.994	0.947	0.280	5.26 E +03	1
PVAc+methanol	353.2	1,67,000	0.660	0.791	0.953	0.953	0.443	3.07 E +01	0.999
PVAc+acetone	313.2	1,67,000	0.636	0.370	0.988	0.915	-0.887	4.42 E +03	1
PVAc+acetone	333.2	1,67,000	0.638	0.637	0.914	0.913	-0.005	1.69 E +01	8.21 E -12
PVAc+acetone	353.2	1,67,000	0.646	0.613	0.913	0.916	-0.117	1.12 E +02	1
PVAc+propylamine	313.2	1,00,000	0.659	0.768	1	0.942	0.381	2.16 E +03	0.550
PVAc+2-propanol	313.2	1,67,000	0.625	0.733	0.959	0.960	0.309	6.12 E +01	1
PVAc+2-propanol	333.2	1,67,000	0.630	0.655	0.943	0.940	0.076	2.71 E +01	3.15 E -05
PVAc+2-propanol	353.2	1,67,000	0.644	0.658	0.940	0.941	0.045	2.01 E +01	0.998
PVAc+chloroform	333.15	1,94,000	0.611	-0.012	0.874	0.872	-2.070	6.37 E +02	1

$$\frac{a_m}{RT} = Q \frac{DD}{1-DD}, \quad (36)$$

$$b_m = \frac{Q}{1-DD} \quad (37)$$

$$Q = \sum \sum x_i x_j \left( b - \frac{a}{RT} \right)_{ij} \quad (38)$$

$$DD = \sum_i x_i \frac{a_i}{b_i RT} \quad (39)$$

$$\left( b - \frac{a}{RT} \right)_{ij} = \frac{1}{2} \left[ \left( b_i - \frac{a_i}{RT} \right) + \left( b_j - \frac{a_j}{RT} \right) \right] (1 - k_{ij}) \quad (40)$$

The capability of two Cubic EoS namely PRSV and SRK combined with vdW1, vdW2, WS plus FH model, and ZM mixing rules for prediction of phase behavior for PVAc + solvent binary solutions were evaluated.

Table III shows the calculated results of absolute average deviations (%AAD) between predicted and experimental bubble point pressure data for PVAc/solvent solutions with various models included in PRSV and SRK, separately combined with different mixing rules.

As can be seen in this table (Table III), we can report the best results with the highest accuracy for any model in a specific solution system with absolute average deviation percent of 0.6, 0.6, 1, 1.2, 0.7, 0.6, 0.9, and 1 for PVAc + acetone with molecular weight of 1,67,000 (g/mol) at 333.2 (K), containing of models PRSV + Vdw1, PRSV + Vdw2, PRSV + WS, PRSV + ZM, SRK + Vdw1, SRK + Vdw2, SRK + WS, and SRK + ZM, respectively.

## RESULTS AND DISCUSSION

In this work, the computational algorithm (Figure 1) was implemented based on bubble point pressure calculations for PVAc/solvent binary solutions at wide range of molecular weight of PVAc and various temperatures of solution systems.

**Table V.** Optimized Adjustable Binary Interaction Parameters Existing in Mixing Rules Used in this Article for SRK CEOS

System	T (K)	MW	$(K_{ij})_{vdW1}$	$(K_{ij})_{vdW2}$	$(K_{ij})_{WS}$	$(K_{ij})_{ZM}$	$(l_{ij})_{vdW2}$	$r$	$\chi$
PVAc+benzene	313.15	1,58,000	0.632	0.690	0.989	0.914	0.180	4.54 E +03	0.99
PVAc+benzene	333.15	1,58,000	0.639	0.759	0.996	0.916	0.381	5.20 E +03	1
PVAc+methanol	313.2	1,67,000	0.651	0.582	0.989	0.956	-0.227	4.54 E +03	0.99
PVAc+methanol	333.2	1,67,000	0.659	0.733	0.995	0.948	0.246	5.53 E +03	1
PVAc+methanol	353.2	1,67,000	0.677	0.803	0.953	0.954	0.450	3.16 E +01	1
PVAc+acetone	313.2	1,67,000	0.654	0.352	0.989	0.917	-1.080	4.54 E +03	0.99
PVAc+acetone	333.2	1,67,000	0.656	0.639	0.916	0.915	-0.059	1.55 E +01	2.17 E -06
PVAc+acetone	353.2	1,67,000	0.663	0.612	0.915	0.918	-0.189	1.12 E +02	1
PVAc+propylamine	313.2	1,00,000	0.676	0.764	1	0.944	0.327	1.25 E +03	8.53 E -07
PVAc+2-propanol	313.2	1,67,000	0.650	0.655	0.943	0.941	0.016	2.57 E +01	2.18 E -06
PVAc+2-propanol	333.2	1,67,000	0.650	0.655	0.943	0.941	0.016	2.57 E +01	2.18 E -06
PVAc+2-propanol	353.2	1,67,000	0.662	0.657	0.940	0.941	-0.017	2.14 E +01	0.999
PVAc+chloroform	333.15	1,94,000	0.659	0.733	0.995	0.948	0.246	5.53 E +03	1

As depicted in this table, although the capability of two equations of state had a good agreement with experimental data and predict the correct type of phase behavior in all cases, the performance of the PRSV + vdW2 led to better results than the other models. The PRSV + vdW2 model was the best predictive model with the highest accuracy (AAD = 2.65%) among the other models. Among these models, the mixing rule of vdW2 with both CEoS had a less deviation with experimental data especially in low solvent weight fraction ( $\leq 0.3$ ). The Zhong and Masuoka (ZM) mixing rule was found as the worst model with the lowest accuracy among the others.

Figure 2 shows the overall result of absolute average deviations between predicted and experimental bubble point pressure data for sum of PVAc/solvent solutions with various models. In this study for more investigated solutions, the detailed analysis of results showed that the PRSV with combination of vdW2 had a higher accuracy than the other models and it was the best model between the others with the lowest overall absolute average deviation.

The calculated vapor–liquid equilibria of some of PVAc/solvent systems are shown graphically in Figures 3–10. Good agreement with experimental data confirms that PRSV and SRK are generally capable for VLE correlation of these solutions.

Figures 3 and 4 show the predictive behavior of models PRSV and SRK for PVAc + 2-propanol at  $T = 333.2$  K with a polymer molecular weight of 1,670,000 g/mol. These figures demonstrate a good agreement between the results obtained from the CEoS models and experimental data for this system. Although all of the models had a very satisfactory result for this solution system, SRK + vdW2 model was the best predictive model with absolute average deviation value of 1.48%.

Figures 5 and 6 show the predictive correlation of models for saturation pressure in PVAc/methanol solution system at  $T = 353.2$  K with a polymer molecular weight of 1,67,000 g/mol. The SRK + vdW2 with accuracy of 0.91% was the best model for this solution system.

The PVAc ( $MW = 1,67,000$ )/acetone (Figures 7 and 8) and PVAc ( $MW = 1,58,000$ )/benzene (Figures 9 and 10) systems in VLE with  $T = 333.2$  K and  $T = 313.15$  K, respectively, can be well described by PRSV + vdW2 with AAD = 0.57% and 1.71%, respectively.

As can be seen in these figures, results show that the CEoS models can accurately correlate the VLE experimental data of (PVAc + solvent) systems over a wide range of temperatures and molecular weight, particularly at low molecular weight of polymers.

The eq. (41), as an objective function was used to optimize the adjustable parameters of CEoS.

$$OF = \frac{1}{N_{\text{exp}}} \sum_{i=1}^{N_{\text{exp}}} \frac{|P_{\text{cal},i} - P_{\text{exp},i}|}{P_{\text{exp},i}} \quad (41)$$

Tables IV and V present the optimized adjustable parameters existing in mixing rules used in this study for PRSV and SRK CEoS, respectively. The binary interaction parameter values ( $k_{ij}$ ) for PRSV + vdW1, PRSV + vdW2, PRSV + WS, and

PRSV + ZM models were in the range of (0.61–0.66), (0.37–0.81), (0.87–1), and (0.87–0.96), respectively. Also, the binary interaction parameter values ( $k_{ij}$ ) for SRK + vdW1, SRK + vdW2, SRK + WS, and SRK + ZM models were in the range of (0.63–0.67), (0.35–0.8), (0.92–1), and (0.91–0.95), respectively. As a result, with our investigation on optimized adjustable parameters, it seems better that use special range of optimized parameter for its solution system. These ranges of data can be a good guideline for future modeling of phase equilibria in other PVAc solution systems with different molecular weight at various temperatures in industrial applications such as separation and purification processes.

## CONCLUSION

Vapor–liquid equilibria of PVAc/solvent solutions have been correlated using CEoS with a high accuracy. The parameters of the cubic EoS were calculated using the vdW2, Wong–Sandler, Zhong–Masuoka, and vdW1 mixing rules, and we used the Flory–Huggins as an excess Gibbs free energy model incorporated in the Wong–Sandler mixing rule. PRSV + vdW2 was selected as the best model compared with the other cubic EoS models. VdW2, vdW1, WS, and ZM mixing rules have all demonstrated their ability to describe phase behavior with the lowest error, respectively. Advantages of this approach are that it extends the CEoS to polymer–solvent systems in a simple fashion by including free volume effect in the excess Gibbs energy. This will allow for accurate interpolation and extrapolation of existing experimental data. The results of these models show very good agreement with experimental data for many binary polyvinyl acetate solutions with different molecular mass and temperature. Finally, the best result of overall absolute average deviation percent for total of solution systems was 2.65 with PRSV + VdW2 model.

## NOMENCLATURE

### List of symbols

$a$	energy or attraction constant
$a_m$	energy or attraction constant of the mixture
$A^E$	molar excess Helmholtz energy
$A_{\infty}^E$	molar excess Helmholtz energy at infinite pressure
$b$	co-volume or excluded volume
$b_m$	co-volume or excluded volume of the mixture
$k_{ij}$	binary interaction parameter
$MW$	molecular weight
$p$	system pressure
$P_c$	critical pressure
$r$	the number of solvent-size segments
$T$	temperature
$T_c$	critical temperature
$T_r$	reduce temperature
$v$	molar volume
$x$	mole fraction of component $i$

### Greek letters

$\chi$	Flory interaction parameter
$\Phi$	volume fraction



$\gamma$  activity coefficient  
 $\omega$  acentric factor  
 $\varphi_i$  fugacity coefficient of a species  $i$

## APPENDIX

With the selection of the PRSVEoS and Wong–Sandler mixing rule, the fugacity coefficient of a species  $i$  in a homogeneous binary mixture is given by Wong and Sandler:<sup>28</sup>

$$\ln \varphi_i = -\ln \left[ \frac{P(v-b)}{RT} \right] + \frac{1}{b_m} \left( \frac{\partial n b_m}{\partial n_i} \right) \left( \frac{Pv}{RT} - 1 \right) + \frac{1}{2\sqrt{2}} \left( \frac{a_m}{RT b_m} \right) \times \left[ \frac{1}{a_m} \left( \frac{\partial n^2 a_m}{\partial n_i} \right) - \frac{1}{b_m} \left( \frac{\partial n b_m}{\partial n_i} \right) \right] \ln \left[ \frac{v + b_m(1-\sqrt{2})}{v + b_m(1+\sqrt{2})} \right]. \quad (\text{A1})$$

The partial derivatives of  $a_m$  and  $b_m$  are:

$$\frac{\partial n b_m}{\partial n_i} = \frac{1}{(1-DD)} \left( \frac{1}{n} \frac{\partial n^2 Q}{\partial n_i} \right) - \frac{Q}{(1-DD)^2} \left( 1 - \frac{\partial n DD}{\partial n_i} \right), \quad (\text{A2})$$

$$\frac{1}{RT} \left( \frac{\partial n^2 a_m}{\partial n_i} \right) = DD \frac{\partial n b_m}{\partial n_i} + b_m \frac{\partial n DD}{\partial n_i}, \quad (\text{A3})$$

With the partial derivatives of  $Q$  and  $DD$  given by:

$$\frac{1}{n} \left( \frac{\partial n^2 Q}{\partial n_i} \right) = 2 \sum x_j \left( b - \frac{a}{RT} \right)_{ij} \quad (\text{A4})$$

$$\frac{\partial n DD}{\partial n_i} = \frac{a_i}{b_i RT} + \frac{\ln \gamma_i}{C}. \quad (\text{A5})$$

The activity coefficient expressions for the Flory–Huggins models are:

$$\ln \gamma_1 = \ln \frac{\Phi_1}{x_1} + \left( 1 - \frac{1}{r} \right) \Phi_2 + \chi \Phi_2^2, \quad (\text{A6})$$

$$\ln \gamma_2 = \ln \frac{\Phi_2}{x_2} + (1-r) \Phi_1 + \chi \Phi_1^2 r. \quad (\text{A7})$$

## REFERENCES

- Tsivintzelis, I.; Kontogeorgis, G. M. *Fluid Phase Equilib.* **2009**, *280*, 100.
- Murray, G. T. *Handbook of Materials Selection for Engineering Applications*, Taylor & Francis Inc: New York/United States, **1997**; p 242.
- O'Neil, M. J.; Smith A.; Heckelman. *Poly(vinyl Acetate)*, 5th ed.; Council of Europe: Strasbourg, France, **2005**; Vol. 2, pp 2271.
- Polyvinyl Acetate—The Leading Polyvinyl Acetate Manufactory. Jiangsu Yinyang Gumbase Materials., Co., Ltd. Available at: [polyvinylacetate.webs.com/applicationsofpvac.htm](http://polyvinylacetate.webs.com/applicationsofpvac.htm). Accessed date 11 April 2012.
- Gupta, R. B.; Prausnitz, J. M. *J. Chem. Eng. Data* **1996**, *40*, 784.
- Se, R. A. G.; Aznar, M. *Polymer* **2007**, *48*, 5646.
- Pasquali, I.; Bettini, R. *Int. J. Pharm.* **2008**, *364*, 176.
- Romero, R. B.; Leite, C. A. P.; do Carmo Gonçalves, M. *Polymer* **2009**, *50*, 161.
- Tsivintzelis, I.; Marras, S. I.; Zuburtikudis, I.; Panayiotou, C. *Polymer* **2007**, *48*, 6311.
- Bong, H. C.; Young, C. B. *Polymer* **2002**, *43*, 6627.
- Hirano, T.; Kamikubo, T.; Fujioka, Y.; Sato, T. *Eur. Polym. J.* **2008**, *44*, 1053.
- Radfarnia, H. R.; Taghikhani, V.; Ghotbi, C.; Khoshkbarchi, M. K. *J. Chem. Thermodyn.* **2004**, *36*, 409.
- Louli, V.; Tassios, D. *Fluid Phase Equilib.* **2000**, *168*, 165.
- Staudt, P. B.; Soares, R. de P.; Secchi, A. R.; Cardozo, N. S. M. *Fluid Phase Equilib.* **2010**, *295*, 38.
- Striolo, A.; Prausnitz, J. M. *Polymer* **2000**, *41*, 1109.
- Lieu, J. G.; Prausnitz, J. M.; Gauthier, M. *Polymer* **2000**, *41*, 219.
- Fornasiero, F.; Halim, M.; Prausnitz, J. M. *Macromolecules* **2000**, *33*, 8435.
- Kruger, K. M.; Pfohl, O.; Dohrn, R.; Sadowski, G. *Fluid Phase Equilib.* **2006**, *241*, 138.
- Voutsas, E.; Kalospiros, N. S.; Tassios, D. *Fluid Phase Equilib.* **1995**, *109*, 1.
- Zhong, C.; Masuoka, H. A. *Fluid Phase Equilib.* **1996**, *123*, 59.
- Voutsas, E.; Magoulas, K.; Tassios, D. *Ind. Eng. Chem. Res.* **2004**, *43*, 6238.
- Wang, L. S. *Fluid Phase Equilib.* **2007**, *260*, 105.
- Prausnitz, J. M.; Lichtenthaler, R. N.; Azevedo, E. G. *Molecular Thermodynamics of Fluid Phase Equilibria*, 2nd ed.; Prentice-Hall: Englewood Cliffs, NJ, 1986.
- Valderrama, J. O. *Ind. Eng. Chem. Res.* **2003**, *42*, 1603.
- Stryjek, R.; Vera, J. H. *Can. J. Chem. Eng.* **1986**, *64*, 323.
- Soave, G. *Chem. Eng. Sci.* **1972**, *27*, 1197.
- Kontogeorgis, M. G.; Fredenslund, A.; Economou, I. G.; Tassios, D. P. *AIChE J.* **1994**, *40*, 1711.
- Wong, S. H.; Sandler, S. I. *AIChE J.* **1992**, *38*, 671.