

Prediction of Vapor-Liquid Equilibrium of Polypropylene Oxide Solution Systems by Cubic Equations of State

Hajir Karimi, Mahmood Reza Rahimi, and Ebrahim Ahmadloo

Abstract—In this research, vapor-liquid equilibrium behavior of Polypropylene oxide (PPO)/solvent and Polypropylene glycol (PPG)/solvent were calculated using cubic equation of states. Eight models containing PRSV and SRK CEOS 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 of absolute average deviations (%AAD) between predicted and experimental bubble point pressure were calculated and presented. The PRSV+vdW2 model was the best predictive model with the highest accuracy (AAD=1.021%) between other models.

Index Terms—Vapor-liquid equilibrium, polypropylene oxide solutions, cubic equations of state.

I. INTRODUCTION

The Phase behavior of polymer solutions are of extreme importance for the development of in several polymer processing and many polymers are produced in solution [1], [2]. The polymer devolatilization and other polymeric membrane separation processes [3], recovery of organic vapors from waste-air streams using a polymeric membrane [4], and pervaporation [5] may be have a few residual solvents.

In such as process we should remove these residual solvents. The removal of solvents is important for polymeric materials used in the food and pharmaceutical industry [6].

In the recent years there has been an increase in publications on the VLE for polymer/solvent systems. Development of accurate thermodynamic models for polymer solutions is also essential in the design of advanced polymeric materials and separation process that employ polymer solutions. Some of models have presented based on the van der Waals theory while several authors [7]-[15] further developed the models according to the lattice base. These bases have been used for the development of various activity coefficient models as well as equations of state [16].

Cubic equations of state (CEOS) are widely used in thermodynamic science for computing phase equilibrium and properties of 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: 1) numeric and analytical procedures for dealing with a great variety of properties calculation and phase equilibrium problems are well established for CEOS; 2) implementations of CEOS are available in most commercial computational packages for thermodynamic applications; 3) 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 [17]–[23].

The objective of this work is predicting of vapor-liquid equilibrium of Polypropylene oxide/solvent solutions by PRSV and SRK cubic equations of state using four mixing rules namely: Van der vaals 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.

II. THERMODYNAMIC MODEL

A. (Vapor + Liquid) Equilibrium Calculation for Polymer Solutions

For the VLE calculations on mixtures, the equal fugacity criterion is employed for each component. The quantity of polymer in the vapor phase is close to zero for polymer solutions,. So, the phase equilibrium equation for solvent in a polymer solution can be expressed as:

$$\phi_1^v P = x_1 \phi_1^l P \quad (1)$$

where ϕ_1^l and ϕ_1^v are the fugacity coefficients of solvent in the liquid and vapor phases, respectively. Therefore, the fugacity coefficient [24] can be obtained in both phases as:

$$RT \ln \phi_i^v = \int_{V^v}^{\infty} \left[\left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_{j \neq i}} - \frac{RT}{P} \right] dV - RT \ln Z_{mix}^v \quad (2)$$

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

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

B. Cubic Equations of State

Most of the CEOS available today are special cases of a generic cubic equation [22], which can be written as:

$$P = \frac{RT}{V-b} - \frac{a(T)}{(V+\epsilon b)(V+\sigma b)} \quad (4)$$

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where ϵ and σ are constants for all substances and depend on the EoS 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:

$$a(T) = \psi \frac{\alpha(T_r, \omega) R^2 T_c^2}{P_c} \quad (5)$$

$$b = \Omega \frac{RT_c}{P_c} \quad (6)$$

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. In fact, variations in values or expressions for $a(T)$ and b are the source for hundreds of cubic EOS available today.

In this work, the polymer parameter a and b are evaluated based on literature [25]. In calculations, where the polymer's molecular weight differs from those of the reference paper [25], 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 I lists the parameter a /MW and b /MW for the CEOS of the PPO(PPG).

TABLE I: CEOS PARAMETERS FOR PPO(PPG) CALCULATED WITH LOULI AND TASSIOS [25]

Polymer	T range (K)	P range (bar)	a /MW	b /MW	AAE% in V
PPO (PPG)	303.15–471.15	0–2000	2,254,648	0.835	1.66

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

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

1) 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 [26].

In this work, PRSV EOS [26] is used as:

$$P = \frac{RT}{v-b} - \frac{a}{v^2 + 2vb - b^2} = \frac{RT}{v-b} - \frac{a}{(v + (1 + \sqrt{2})b)} \quad (7)$$

$$a = 0.457235 \frac{R^2 T_c^2}{P_c} \alpha \quad (8)$$

$$b = 0.077796 \frac{RT_c}{P_c} \quad (9)$$

$$\alpha = [1 + k(1 - T_r^{0.5})]^2 \quad (10)$$

The modification is:

$$k = k_0 + k_1(1 + T_r^{0.5})(0.7 - T_r) \quad (11) \quad k_0 = 0.378893 + 1.4897153\omega - 0.17131848\omega^2 + 0.0196554\omega^3$$

$$T_r = \frac{T}{T_c} \quad (12)$$

where k_1 , ω 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 [26]. To estimating of Z_{mix} , the PRSV EOS can be written as follows:

$$Z_{\text{mix}}^3 - (1 - B)Z_{\text{mix}}^2 + (A - 3B^2 - 2B)Z_{\text{mix}} - (AB - B^2 - B^3) = 0 \quad (13)$$

$$A = \frac{a_{\text{mix}} P}{R^2 T^2} \quad (14)$$

$$B = \frac{b_{\text{mix}} P}{RT} \quad (15)$$

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

2) SRK EoS

In this work, SRK EOS [27] is used as:

$$P = \frac{RT}{v} - \frac{a}{v(v+b)} \quad (16)$$

$$a = 0.42747 \frac{R^2 T_c^2}{P_c} \alpha \quad (17)$$

$$b = 0.08664 \frac{RT_c}{P_c} \quad (18)$$

$$\alpha = [1 + (0.48508 + 1.55171\omega - 0.15613\omega^2)(1 - T_r^{0.5})]^2 \quad (19)$$

To estimating of Z_{mix} , the PRSV EOS can be written as follows:

$$Z_{\text{mix}}^3 - Z_{\text{mix}}^2 + (A - B - B^2)Z_{\text{mix}} - AB = 0 \quad (20)$$

C. Mixing Rules

The ability of a CEOS to correlate and predict phase equilibria of mixtures depends strongly upon the mixing rule applied. Among Several mixing rules suggested, the following are the most popular and adopted methods were chosen to test the ability of the EoS to predicative of phase equilibria behavior in polymer solutions.

1) 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. This rule is capable of accurately representing vapor-liquid equilibria using only one binary-interaction parameter for non-polar or slightly polar systems.

$$a = \sum \sum x_i x_j a_{ij}, \quad (21)$$

$$b = \sum x_i b_i, \quad (22)$$

$$a_{ij} = \sqrt{a_i a_j} (1 - k_{ij}) \quad (23)$$

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.

2) vdW2 mixing rule

The second mixing rule is the conventional two-parameter van der Waals one-fluid mixing rule (vdW2) [28]:

$$a = \sum \sum x_i x_j a_{ij}, \quad (24)$$

$$b = \sum \sum x_i x_j b_{ij}, \quad (25)$$

$$a_{ij} = \sqrt{a_i a_j} (1 - k_{ij}), \quad (26)$$

$$b_{ij} = \frac{b_i + b_j}{2} (1 - l_{ij}) \quad (27)$$

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 l_{ij} , like k_{ij} can be obtained from the regression of VLE.

3) Wong-sandler mixing rule

In this mixing rule, 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:

$$b_m = \frac{Q}{1-DD}, \quad (28)$$

$$\frac{a_m}{RT} = Q \frac{DD}{1-DD}, \quad (29)$$

$$Q = \sum \sum x_i x_j \left(b - \frac{a}{RT} \right)_{ij}, \quad (30)$$

$$\left(b - \frac{a}{RT} \right)_{ij} = \frac{1}{2} \left[\left(b_i - \frac{a_i}{RT} \right) + \left(b_j - \frac{a_j}{RT} \right) \right] (1 - k_{ij}) \quad (31)$$

$$DD = \sum x_i \frac{a_i}{b_i RT} + \frac{A_{\infty}^E}{CRT}, \quad (32)$$

where C is a constant equal to $(1/\sqrt{2})\ln(\sqrt{2} - 1)$ and A_{∞}^E is any suitable molar excess Helmholtz energy model at infinite pressure or equivalently an excess Gibbs energy model at low pressure. 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

$$\frac{A^E}{RT} = x_1 \ln \frac{\phi_1}{x_1} + x_2 \ln \frac{\phi_2}{x_2} + \chi \phi_1 \phi_2 (x_1 + x_2 r) \quad (33)$$

Here, χ is the Flory interaction parameter, Φ 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.

4) Zhong and Masuoka mixing rule

Zhong and Masuoka [21] came up with a new mixing rule for extending cubic EoS to polymer solutions, refining the work done by Wong-Sandler [29]. Actually, the only difference between this mixing rule and the Wong-Sandler one is the absence of excess Helmholtz energy at infinite pressure, A_{∞}^E , which was set equal to zero in this case.

$$\frac{a_m}{RT} = Q \frac{DD}{1-DD}, \quad (34)$$

$$b_m = \frac{Q}{1-DD} \quad (35)$$

$$Q = \sum \sum x_i x_j \left(b - \frac{a}{RT} \right)_{ij} \quad (36)$$

$$DD = \sum \sum x_i x_j \left(b - \frac{a}{RT} \right)_{ij} \quad (37)$$

$$\left(b - \frac{a}{RT} \right)_{ij} = \frac{1}{2} \left[\left(b_i - \frac{a_i}{RT} \right) + \left(b_j - \frac{a_j}{RT} \right) \right] (1 - k_{ij}) \quad (38)$$

III. RESULTS AND DISCUSSION

In this work, the computational algorithm were implemented based on bubble point pressure calculations for Polypropylene oxide/solvent binary solutions at wide range of molecular weight of PPO(PPG) and various temperatures of solution systems. The capability of two Cubic EoS namely PRSV and SRK combined with vdW1, vdW2, WS plus FH model and ZM mixing rules to prediction of phase behavior for PPO(PPG)+solvent binary solutions were evaluated.

Table II shows the calculated results of absolute average deviations (%AAD) between predicted and experimental bubble point pressure data for PPO(PPG)/solvent solutions with various models included in PRSV and SRK, separately combined with different mixing rules. It is noted that experimental data points are collected from the literatures [30], [31].

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, but the performance of the PRSV+ vdW2 was more reliable than the other models. The PRSV+vdW2 model was the best predictive model with the highest accuracy (AAD=1.021%) between other models. Among of these models the vdW2 mixing rule with both CEOS had a less deviation with experimental data especially in low solvent weight fraction (≤ 0.3). The Zhong and Masuoka(ZM) mixing rule was found as the worst model with the lowest accuracy between the others.

The calculated vapor-liquid equilibrium for some of PPO(PPG)/solvent systems is shown graphically in Fig. 1 to Fig. 4. Good agreement with experimental data confirms that these PRSV and SRK are generally capable for VLE correlation of these solutions.

Fig. 1 and Fig. 2 show the predictive behavior of models basis PRSV and SRK for PPG+ N-Hexane at $T=323.15K$ with a polymer molecular weight of 500 gr/mol.

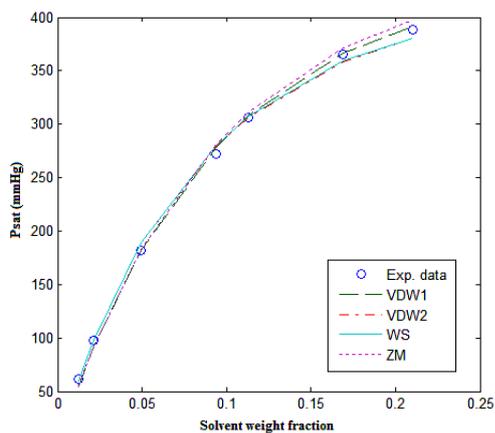


Fig. 1. Prediction of the bubble point pressure for systems containing PPG(MW =500)+ N-Hexane at ($T=323.15\text{K}$) with PRSV EOS models.

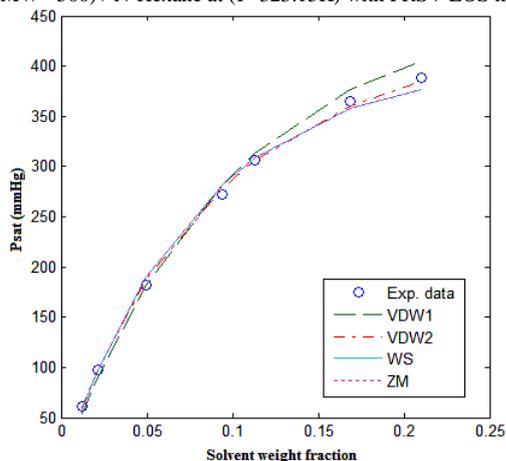


Fig. 2. Prediction of the bubble point pressure for systems containing PPG(MW =500)+ N-Hexane at ($T=323.15\text{K}$) with SRK EOS models.

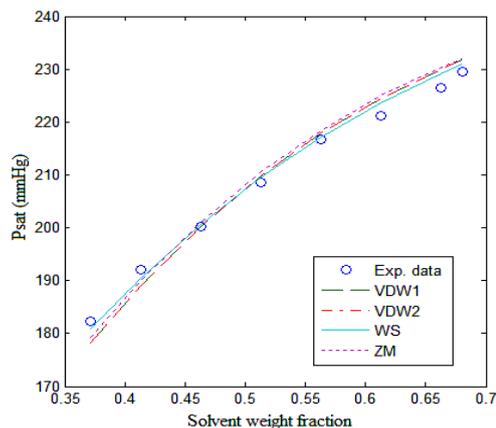


Fig. 3. Comparison of the calculated results of bubble point pressure with experimental data for systems containing PPO(MW=500000)+Benzene at ($T=320.35\text{K}$) with PRSV EOS models.

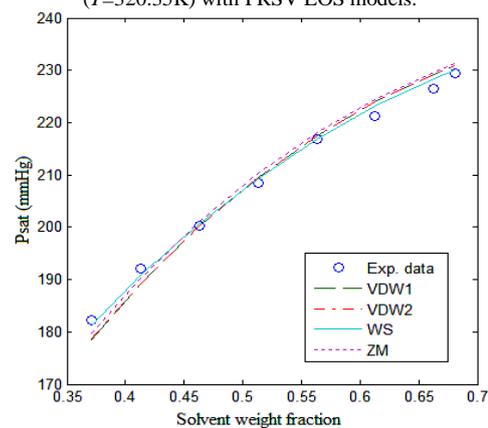


Fig. 4. Comparison of the calculated results of bubble point pressure with experimental data for systems containing PPO(MW =500000) + Benzene at ($T=320.35\text{K}$) with SRK EOS models.

TABLE II: CALCULATED RESULTS OF ABSOLUTE AVERAGE DEVIATIONS (%AAD) BETWEEN PREDICTED AND EXPERIMENTAL BUBBLE POINT PRESSURE DATA FOR PPG(PPO) / SOLVENT SOLUTIONS WITH VARIOUS MODELS CONTAINING PRSV AND SRK CEOS COMBINING WITH DIFFERENT MIXING RULES

NO.	System	Ref.	T(K)	MW(g mol ⁻¹)	NP	AAD (%)							
						PRSV				SRK			
						Vdw1	Vdw2	WS	ZM	Vdw1	Vdw2	WS	ZM
1	PPG+Water	[31]	303.15	400	6	2.992	1.359	16.432	26.894	3.336	2.109	13.905	25.144
2	PPG+N-Hexane	[31]	323.15	400	6	2.178	1.623	15.767	26.861	3.191	1.869	12.083	24.107
3	Hexane	[31]	312.65	500	7	2.869	2.567	2.720	6.248	2.983	2.563	2.728	2.783
4	PPG+N-Hexane	[31]	323.15	500	7	2.559	1.824	0.932	3.724	2.587	1.445	1.088	2.525
5	Hexane	[30]	320.35	500000	8	1.107	1.107	0.655	1.165	0.909	0.899	0.460	0.959
6	PPO+Benzene	[30]	333.35	500000	11	0.212	0.208	0.240	0.210	0.221	0.220	0.242	0.220
7	PPO+Benzene	[30]	343.05	500000	9	0.352	0.342	0.522	0.372	0.483	0.463	0.535	0.470
8	PPO+Benzene	[30]	347.85	500000	13	0.471	0.426	0.829	0.562	0.468	0.451	0.859	0.646
Overall deviation					67	1.336	1.021	3.614	6.189	1.467	1.068	3.06	5.304

$$\text{AAD}\% = \frac{\Delta P}{P} \% = 100 \times \sum_{i=1}^{NP} \frac{|P_{cal,i} - P_{exp,i}|}{P_{exp,i}}; \text{ NP, number of data points.}$$

These figures demonstrate a good agreement between the results obtained from the CEOS model and experimental data for this system. Although In this solution system all of models had a very satisfactory result but the PRSV+WS model with value of 0.93% in absolute average deviation of bubble point pressure with experimental data was the best predictive model.

The PPO (MW=500000)/ Benzene (Fig. 3 and Fig. 4) solution systems VLE with $T=320.35\text{K}$ can be well described by SRK+WS with AAD of 0.46%.

As can be seen in these figures, results show that the

CEOS models can accurately correlate the VLE experimental data of (PPO(PPG) + solvent) systems over a wide range of temperatures and molecular weight, particularly at low molecular weight of polymers.

The Eq. (39), as an objective function was used to optimize the adjustable parameters of CEOS.

$$\text{OF} = \frac{1}{N_{exp}} \sum_{i=1}^{N_{exp}} \frac{|P_{cal,i} - P_{exp,i}|}{P_{exp,i}} \quad (39)$$

Table III and Table IV 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 (0.13-0.63), (0.13-0.68), (0.52-1) and (0.64-0.98), 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 (0.05-0.65), (0.06-0.64), (0.47-1) and (0.52-0.98), respectively.

IV. CONCLUSION

Vapor-liquid equilibrium of PPO(PPG)/solvent solutions have been correlated using cubic equation of state 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 Florry-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 cubic equation of state 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 the present models show very good agreement with experimental data for many binary Polypropylene oxide solutions with different molar mass and temperature.

TABLE III: OPTIMIZED ADJUSTABLE BINARY INTERACTION PARAMETERS EXISTING IN MIXING RULES USED IN THIS PAPER FOR PRSV CEOS

System	T (K)	MW	(K_{ij}) _{vdw1}	(K_{ij}) _{vdw2}	(K_{ij}) _{ws}	(K_{ij}) _{ZM}	(I_{ij}) _{vdw2}	R	X
PPG+water	303.15	400	0.509231	0.50915	0.976289	0.985946	-0.0025	1.64E+00	1
PPG+water	323.15	400	0.514914	0.511443	0.965183	0.97594	-0.02498	1.76E+00	1
PPG+n-hexane	312.65	500	0.134586	0.136328	0.520168	0.672404	-0.0165	3.36E+00	0.764948
PPG+n-hexane	323.15	500	0.128794	0.132452	0.60743	0.641806	-0.02008	1.00E+00	0.13438
PPO+benzene	320.35	500000	0.625961	0.627693	1	0.871221	0.005344	7.10E+03	7.92E-08
PPO+benzene	333.35	500000	0.632968	0.657091	0.979577	0.880809	0.075996	9.00E+03	0.288859
PPO+benzene	343.05	500000	0.634133	0.651624	0.986475	0.879566	0.05608	1.44E+04	0.584575
PPO+benzene	347.85	500000	0.634632	0.689476	0.987696	0.879927	0.175819	1.54E+04	0.607484

TABLE IV: OPTIMIZED ADJUSTABLE BINARY INTERACTION PARAMETERS EXISTING IN MIXING RULES USED IN THIS PAPER FOR SRK

System	T (K)	MW	(K_{ij}) _{vdw1}	(K_{ij}) _{vdw2}	(K_{ij}) _{ws}	(K_{ij}) _{ZM}	(I_{ij}) _{vdw2}	R	X
PPG+water	303.15	400	0.50763	0.506628	0.977779	0.988713	-0.03846	1.64E+00	1
PPG+water	323.15	400	0.512742	0.507631	0.961777	0.974805	-0.06191	1.80E+00	1
PPG+n-hexane	312.65	500	0.056807	0.058831	0.472465	0.554716	-0.01773	3.26E+00	0.586657
PPG+n-hexane	323.15	500	0.048724	0.052955	0.522793	0.521207	-0.02039	1.11E+00	1.33E-13
PPO+benzene	320.35	500000	0.645239	0.619848	1	0.878347	-0.08394	6.96E+03	2.43E-14
PPO+benzene	333.35	500000	0.65109	0.64159	0.979881	0.884861	-0.03209	8.91E+03	0.275297
PPO+benzene	343.05	500000	0.651601	0.632635	0.986749	0.883189	-0.06493	1.44E+04	0.567199
PPO+benzene	347.85	500000	0.651987	0.627337	0.987852	0.883248	-0.0847	1.51E+04	0.571119

APPENDIX

List of symbols

a	energy or attraction constant
a_m	energy or attraction constant of the mixture
A^E	molar excess Helmholtz energy
A_{∞}^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

χ	Flory interaction parameter
Φ	volume fraction

γ	activity coefficient
ω	acentric factor
ϕ_i	fugacity coefficient of a species i

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