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Prediction of Critical Properties of Binary Mixtures Using the PRSV-2 Equation of State

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The aim of this work is to test the value of the Peng–Robinson–Stryjek–Vera (PRSV-2) equation of state for predicting the critical behavior of binary mixtures. A procedure adopted by Heidemann and Khalil, based on the Helmholtz free energy, has been followed. The resulting two complex nonlinear equations have been solved simultaneously for the critical temperature and volume, while the critical pressure is calculated from the PRSV-2 equation of state itself. Three forms of binary-interaction parameters have been tried: the zero-type, conventional one-parameter type, and Margules two-parameter type. The optimum values of the binary interaction parameters, based on minimizing the sum of the squares of the relative errors between predicted and experimental critical temperatures, have been calculated for 20 polar and nonpolar systems. The Margules two-parameter type gives the best results, but its mathematical derivation is cumbersome and it requires more computation time. The standard and the average of the absolute relative deviations in critical properties are included. The predicted critical temperatures and pressures agree well with the experimental results, and are always better than those predicted by the group-contribution method. The deviations in the predicted critical volumes using any of the tested binary-interaction parameter types are relatively large compared to those using the group-contribution method.

KEY WORDS: binary mixtures; critical properties; equation of state.

1. INTRODUCTION

Critical properties of fluids or fluid mixtures are important for describing fluid phase behavior, predicting physical properties, developing equations

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of state, and designing supercritical-fluid extraction processes and compression and refrigeration units [1]. For commonly used pure substances, these critical constants have been determined experimentally. Besides direct measurements, critical properties of mixtures are often estimated on the basis of various correlating methods. Spencer et al. [2] have reviewed these methods in terms of their estimation procedure and accuracy. Li and Kiran [3] divided the bases of the existing correlating methods, available till 1973, into six groups and give references on each of them. These groups are the (a) graphical approach, (b) equation-of-state approach, (c) excess-property approach, (d) conformal solution (corresponding-states principle) approach, (e) thermodynamic-potential approach, and (f) group-contribution approach.

The prediction of true critical properties of multicomponent systems is an important aspect of the general problem of predicting the overall phase behavior of a system. Knowledge of the critical behavior of mixtures is important to determine the existing phase conditions or permissible operating ranges in reactors and mass transfer equipment.

Fluid-property predictions and design calculations in the critical region are often the most difficult to make, and knowledge of the precise location of the critical point for the system under study is of utmost importance. Also in the critical region, the vapor–liquid equilibrium calculations are usually slowly converging. Moreover, the possible occurrence of liquid formation in a compressor necessitates knowledge of whether a given mixture is a vapor, a liquid, or a two-phase mixture.

In enhanced oil recovery processes, the amount of carbon dioxide or intermediate-weight hydrocarbon gas to be added to the recycled separator gas to achieve first-contact or multicontact miscibility with the oil in the well can be estimated by calculating the critical composition at a fixed pressure. Prediction of the critical properties, therefore, is important in modeling the phase behavior exhibited by these mixtures for the simulation of such processes [4].

Because at the critical point density differences between phases vanish, the rate of volume change with respect to pressure becomes infinite, and an infinitesimal temperature gradient can be responsible for a transition from 100% liquid to 100% vapor; the critical condition is difficult to measure accurately [5].

Although experimental critical properties are available for commonly used pure substances and mixtures, experimental investigation of critical properties of every possible fluid mixture is impractical because of the limitations in terms of time and cost. Even though experimental data for some mixtures are available, the data points sometimes may not cover the entire composition range of interest.

Evaluation of critical points for multicomponent mixtures based on an equation of state has attracted considerable attention in recent years. In this approach the second and third derivatives of the molar free energy with respect to composition at constant temperature and pressure must be equal to zero. Determination of the critical properties for mixtures involves the simultaneous solution of an extended form of these derivatives and an equation of state. Joffe and Zudkevitch [6] used the Redlich–Kwong equation of state to predict the critical properties, using a graphical procedure to solve the two simultaneous equations, and the results of their sample calculations indicate that critical temperatures calculated by this approach agree very well with experimental data, but only fair agreement is observed between predicted and experimental critical volumes and pressures. Spear et al. [7] also used the Redlich–Kwong equation of state, but they used a numerical search procedure to carry out the necessary calculations. In general, qualitative results were obtained for the critical properties of binary mixtures, with no empirical adjustment of the interaction parameters.

The first general rigorous procedure for direct determination of critical temperature and pressure was developed by Peng and Robinson [5], who used a criterion based on the Gibbs free energy. This method has been used to predict the critical properties of a total of 32 multicomponent mixtures. Their equation predicts the critical temperature and pressure with an absolute error of about 1.31 and 1.41%, respectively, for natural gas mixtures.

Huron [8] and Huron et al. [9] used the Soave–Redlich–Kwong equation of state and found that the critical points and vapor–liquid equilibria are correctly represented if the interaction parameters are used for binary mixtures consisting of H_2S or CO_2 and C_1 to C_{10} hydrocarbons.

Heidemann and Khalil [10] developed a method based on the Helmholtz free energy and used the Soave–Redlich–Kwong equation of state just to present their method of calculation. To reduce the computational time involved in that method, Michelsen and Heidemann [11] described a computational modification applicable to simple, two-constant cubic equations of state.

Michelsen [12] proposed a method for rapid construction of the complete phase envelope which yields, in addition to the critical point, the retrograde behavior. He also proposed an alternative approach to that of Heidemann and Khalil [10] based on Gibbs' criterion which requires only the first derivative of fugacities with respect to composition.

Teja et al. [13] used the Teja–Patel and the Peng–Robinson equations of state to predict the critical properties of mixtures using the Heidemann and Khalil procedure [10]. These two equations gave very similar results and required similar values of the binary interaction parameters to fit the critical curves. However, they gave poor predictions of the critical volumes, especially at high concentrations of fluids whose critical compressibilities differ from those obtained from the Teja–Patel and the Peng–Robinson equations of state.

Mainwaring et al. [14] used Deiters' equation of state to calculate the critical properties of over 50 binary mixtures and used the Guggenheim equation for comparison purposes. They found that Deiters' equation gives good results for mixtures of moderately different size molecules, whereas Guggenheim's equation is superior for dissimilar size molecules.

Garcia-Sanchez et al. [15] used the simplified perturbed hard-chain-theory equation of state to analyze its ability for the prediction of the critical points of reservoir fluids using the procedure of Heidemann and Khalil [10]. The performance of this equation was demonstrated for four oil reservoir fluid systems containing up to 48 components.

The Heidemann–Khalil method [10], compared to the Peng–Robinson rigorous method [5], is far superior: it is much more efficient, requires less computational effort, and does not need the evaluation of a very large number of high-order determinants. Also, the partial derivatives required using the Helmholtz free energy concept are much more rapidly evaluated than those using the Gibbs free energy concept [11].

2. APPLICATION OF THE HEIDEMANN–KHALIL APPROACH TO THE PRSV-2 EQUATION OF STATE

The Peng–Robinson–Stryjek–Vera (PRSV-2) equation of state has been successfully used for vapor–liquid equilibrium calculations over a wide range of temperatures and yields a good representation of the saturation pressure of pure compounds even at low reduced temperatures [16, 17]. Therefore, the PRSV-2 equation of state has been chosen here to test its ability to predict the critical properties of binary mixtures following the Heidemann and Khalil approach [10]. The Peng–Robinson equation of state in its modified form is given by

$$P = RT/(v-b) - a(T)/\{v(v+b)+b(v-b)\} \tag{1}$$

with pure-compound parameters

$$a = \alpha[0.457235(RT_c)^2/P_c] \tag{2}$$

$$b = 0.077796RT_c/P_c \tag{3}$$

$$\alpha = [1+\kappa(1-T_r^{0.5})]^2 \tag{4}$$

$$\kappa = \kappa_0 + [\kappa_1 + \kappa_2(\kappa_3 - T_r)(1-T_r^{0.5})](1+T_r^{0.5})(0.7-T_r) \tag{5}$$

$$\kappa_0 = 0.378893 + 1.4897153\omega - 0.17131848\omega^2 + 0.0196544\omega^3 \tag{6}$$

The pure-compound critical properties (P_c, T_c, ω) and the pure-component parameters κ_1, κ_2, and κ_3 have been taken from Stryjek and Vera [16, 17] and Proust and Vera [18]. For mixtures, the following mixing rules have been applied:

$$a = \sum_i^N \sum_j^N x_i x_j a_{ij} \tag{7}$$

and

$$b = \sum_i^N x_i b_i \tag{8}$$

For the cross parameter, a_{ij}, the following expressions have been used.

(a) Zero-interaction parameter form:

$$a_{ij} = (a_{ii} a_{jj})^{0.5} \tag{9}$$

(b) Conventional one-binary interaction parameter form:

$$a_{ij} = (a_{ii} a_{jj})^{0.5} (1 - k_{ij}) \tag{10}$$

(c) Margules-type two-binary interaction parameter form:

$$a_{ij} = (a_{ii} a_{jj})^{0.5} (1 - x_i k_{ij} - x_j k_{ji}) \tag{11}$$

where k_{ij} is the binary interaction parameter between component i and component j. The optimized values of k_{ij} for all the studied systems are listed in Appendix B. The optimization procedure is based on the minimization of the sum of the squares of the relative errors in the critical temperature for a given set of data.

In terms of the compressibility factor, Z, Eq. (1) becomes

$$Z^3 - (1 - B) Z^2 + (A - 3B^2 - 2B) Z - (AB - B^2 - B^3) = 0 \tag{12}$$

where $A = aP/(RT)^2$ and $B = bP/RT$.

Equation (12), as a cubic equation, gives three roots for Z: either all real or one real and two complex conjugate roots. When applied to mixtures, the largest positive real root is taken as the value of Z when the mixture is in the vapor phase, while the smallest positive real root is taken for Z when the mixture is in the liquid phase. A single positive real root (or three equal positive real roots) in a given phase means that a pure component exists.

The fugacity of component i as a function of temperature, volume, and mole numbers derived from the PRSV-2 equation is [19]

$$\ln f_i = \frac{b_i}{b_m}(Z-1) - \ln\{(Z-B)/x_i P\} - \frac{A}{2\sqrt{2}\,B}\left(\frac{2\sum x_j a_{ij}}{a_m} - \frac{b_i}{b_m}\right)\ln\left(\frac{Z+(1+\sqrt{2})\,B}{Z+(1-\sqrt{2})\,B}\right) \tag{13}$$

where x_i is the mole fraction of component i in the mixture.

If the Helmholtz free energy is expanded around some test point $(T_0, V_0, n_{10}, n_{20}, ..., n_{N0})$ according to the approach of Heidemann and Khalil [10], one gets

$$\left[A - A_0 - \sum_i^N (\partial A/\partial n_i)\,\Delta n_i\right] = \frac{1}{2}\sum_j^N \sum_i^N (\partial^2 A/\partial n_j\,\partial n_i)\,\Delta n_i\,\Delta n_j + \frac{1}{3!}\sum_k^N \sum_j^N \sum_i^N (\partial^3 A/\partial n_k\,\partial n_j\,\partial n_i)\,\Delta n_i\,\Delta n_j\,\Delta n_k + O(\Delta n^4) \tag{14}$$

The stability of the test point is assured if the quadratic term in Eq. (14) is positive-definite, i.e., equals zero. At such a point, the stability is determined by the properties of the cubic and higher-order terms in Eq. (14). If we note that

$$(\partial A/\partial n_i)\,|_{T,\,v,\,n_j \neq n_i} = RT \ln f_i \tag{15}$$

then the derivative elements in the quadratic and cubic terms in Eq. (14), at constant P, T, and $n_j \neq n_i$, become

$$(\partial^2 A/\partial n_j\,\partial n_i) = RT\{\partial \ln f_i/\partial n_j\} \tag{16}$$

and

$$(\partial^3 A/\partial n_k\,\partial n_j\,\partial n_i) = RT\{\partial^2 \ln f_i/\partial n_k\,\partial n_j\} \tag{17}$$

That is, the first and second partial derivatives of fugacity with respect to the number of moles of constituents j and k have to be evaluated. The expressions that have been reached for these derivatives, on the basis of the PRSV-2 equation of state with conventional mixing rules, are summarized in Appendix A for reference.

The necessary condition for a point to lie on the limit of stability is that the matrix Q with elements

$$q_{ij} = \partial^2 A/\partial n_j\,\partial n_i\,|_{T,\,v} = RT\{\partial \ln f_i/\partial n_j\}\,|_{T,\,v} \tag{18}$$

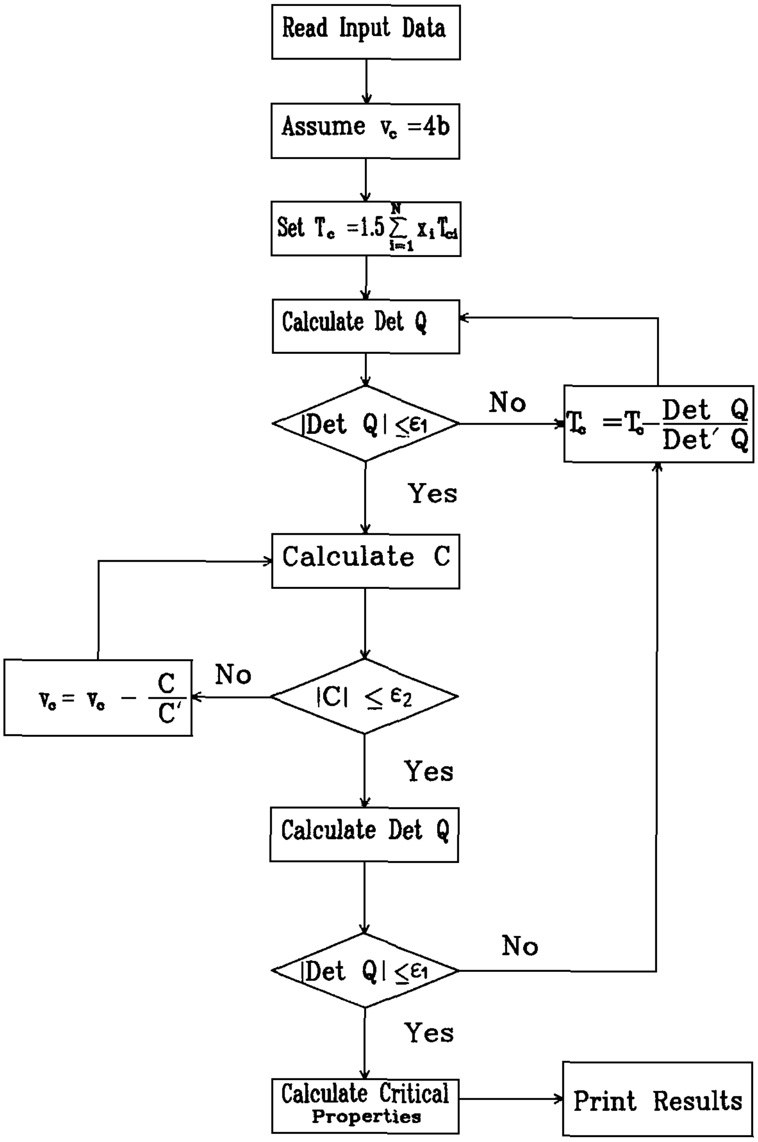

Fig. 1. Schematic flowchart for the calculation procedure of the critical properties of a mixture.

should have a zero determinant, i.e.,

$$\det(Q) = 0 \tag{19}$$

and the cubic term in Eq. (14) must vanish, i.e.,

$$C = \sum_{k}^{N} \sum_{j}^{N} \sum_{i}^{N} \{\partial^2 \ln f_i / \partial n_k \, \partial n_j\} \, \Delta n_i \, \Delta n_j \, \Delta n_k = 0 \tag{20}$$

The resulting two nonlinear equations, Eqs. (19) and (20), have been solved simultaneously for the critical temperature and volume. The critical pressure is then calculated from the PRSV-2 equation of state itself. The computational procedure described by Heidemann and Khalil [10] is followed exactly. A flowchart of the calculation procedure is shown in Fig. 1. For more details see Ref. 19. The experimental critical data used in this work are those of Hicks and Young [20]. The pure-component properties have been taken from Stryjek and Vera [16–18]. The data of Reid et al. [21] have been used for the pure-component properties that are not available in Refs. 16–18.

3. RESULTS AND DISCUSSION

The algorithm described above has been applied to the PRSV-2 equation of state to predict the critical properties of about 24 binary mixtures. Among these systems are paraffins, aromatics, alcohols, ethers, hydrogen sulfide, sulfur dioxide, carbon dioxide, nitrogen, oxygen, hydrogen chloride, and ammonia. The pure-component properties of the systems studied in this work are listed in Table AI (Appendix B). The calculated optimum values of the binary interaction parameters for the systems studied are listed in Tables AII and AIII (Appendix B) for the conventional type and the Margules type, respectively. The criteria used to compare predicted and experimental critical properties are the standard deviation (SD) and the average of the absolute relative deviations (AD) defined below.

$$\mathrm{SD} = \left[\sum_{i}^{M} (\text{exp. value} - \text{calc. value})^2 / (M - 1) \right]^{0.5} \tag{21}$$

$$\mathrm{AD} = \left[\sum_{i}^{M} |\text{exp. value} - \text{calc. value}| / \text{exp. value} \right] \times 100/M \tag{22}$$

where M is the number of points in a given set of data.

It is first noted that all systems studied have continuous critical curves, and the critical locus of each of these systems exhibits a critical temperature

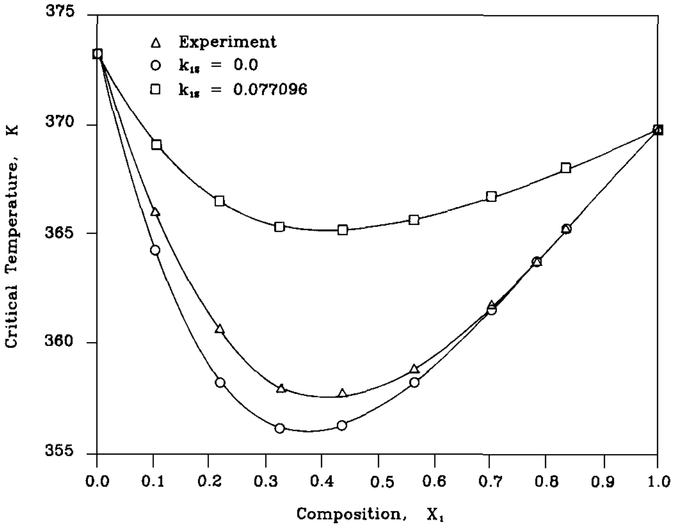

Fig. 2. Critical temperature versus composition for a propane(1)-H_2S(2) mixture.

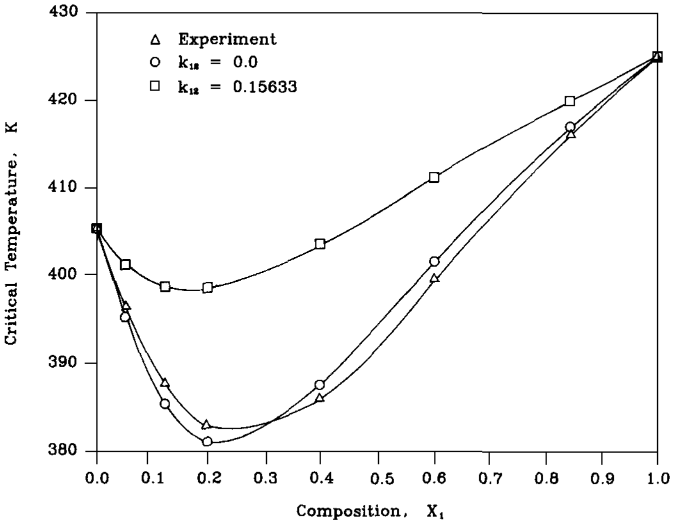

Fig. 3. Critical temperature versus composition for a butane(1)–ammonia(2) mixture.

that varies monotonically with composition. A point of minimum critical temperature has been noted on the critical loci of propane–hydrogen sulfide and butane–ammonia mixtures (see Figs. 2 and 3). This minimum critical temperature is an indication of the formation of a positive azeotrope, i.e., an azeotrope with a minimum in its boiling temperature [22].

Using a conventional one-binary interaction parameter type, we give in Table I the SD and the AD in critical temperature and pressure for some nonpolar systems. For the systems listed in Table I, the average value of the standard deviations is 0.4 K for the critical temperature (with a maximum of about 1.0 K) and 0.5 bar for the critical pressure (with a maximum of about 1 bar). Note that the uncertainties in the experimental values are typically about 0.6 K for the critical temperature and 0.2 bar for the critical pressure [13]. On the other hand, the average value of AD for the systems listed in Table I is about 0.1% for the critical temperature (with a maximum of 0.3%) and about 1.2% for the critical pressure (with a maximum of 2.2%). Table I also shows that using a zero-interaction parameter type, the average values of SD and AD in the critical temperature and pressure are 1.8 K and 0.4% and 0.6 bar and 1.3%, respectively.

Table I. Standard and Average of the Absolute Relative Deviations in Critical Properties for Some Nonpolar Mixtures Using the PRSV-2 Equation of State with Conventional One-Parameter Mixing Rules[a]

		T_c		P_c	
Mixture	M	SD (K)	AD (%)	SD (bar)	AD (%)
Methane–ethane	8	0.942	0.277	1.055	1.212
		1.818	0.564	0.962	1.103
Hexane–heptane	9	0.128	0.018	0.245	0.779
		0.227	0.039	0.253	0.804
Hexane–decane	9	0.895	0.121	0.706	0.236
		2.459	0.401	0.683	2.219
Hexane–cyclohexane	9	0.261	0.037	0.229	0.593
		2.023	0.354	0.360	0.928
Nonane–cyclohexane	9	0.116	0.014	0.688	1.927
		3.383	0.519	0.855	2.227
Nitrogen–oxygen	7	0.259	0.145	0.215	0.259
		0.749	0.460	0.238	0.187
Average for all systems		0.434	0.102	0.523	1.155
		1.788	0.397	0.559	1.245

[a] First line: one-parameter type (κ_{12} listed in Table AII). Second line: zero-parameter type ($\kappa_{12} = 0$).

For some polar systems, the SD and AD in critical properties are shown in Table II on the basis of conventional mixing rules. The average value of SD in the critical temperature for the systems listed in Table II is 1.2 K (with a maximum of 2.2 K). The average value of SD in the critical pressure for the last four systems listed in Table II is 4.6 bar (with a maximum of about 7.3 bar). On the other hand, the average value of AD is 0.2% in the critical temperature (with a maximum of 0.4%) and 5.6% in the critical pressure (with a maximum of about 8.7%).

The effect of using a two-parameter Margules-type mixing rule on the predictive capability of the PRSV-2 equation of state has also been studied. Table III shows a comparison between the calculated SD and AD for PRSV-2 with Margules two-parameter-type, PRSV-2 with conventional one-parameter-type, and PRSV-2 with zero-parameter-type rules, and those of the work of Li and Kiran [3], which are based on the group-contribution method. The method of Li and Kiran does not need experimentally adjusted interaction parameters to predict the critical properties. It is clear that the prediction of the critical temperature is always much better on the basis of the PRSV-2 equation of state. Regarding the above-mentioned four methods in order, the average values of AD for all systems listed in Table III are 0.2, 0.3, 1.4, and 1.7% for the critical temperature, 3.1, 2.6, 3.3, and 10.5% for the critical pressure, and 17.1, 16.8, 17.3, and 3.8% for the critical volume. It is evident that the Margules two-parameter-type rule gives, on the average, slightly better predictions than the conventional type.

Table II. Standard and Average of the Absolute Relative Deviations in Critical Properties for Some Polar Mixtures Using the PRSV-2 Equation of State with a Conventional One-Binary Interaction Parameter[a]

		T_c		P_c		V_c	
Mixture	M	SD (K)	AD (%)	SD (bar)	AD (%)	SD ($ml \cdot mol^{-1}$)	AD (%)
Acetone–benzene	6	1.16	0.17	—	—	—	—
Hexafluorobenzene–decane	8	2.15	0.33	—	—	—	—
Ethanol–water	8	1.04	0.15	—	—	—	—
Benzene–toluene	9	0.31	0.04	0.07	0.13	—	—
Propane–HCl	5	1.10	0.24	4.20	5.66	—	—
Benzene–methanol	5	0.85	0.12	7.26	8.73	48.2	25.1
Butane–Ammonia	6	1.92	0.42	6.75	7.98	32.2	23.1
Average for all systems		1.22	0.21	4.57	5.62	40.2	24.1

[a] Using κ_{12} values listed in Table AII.

Table III. Standard and Average of the Absolute Relative Deviations in Critical Properties Using the PRSV-2 Equation of State with Different Mixing Rules[a]

		T_c		P_c		V_c	
Mixture	M	SD (K)	AD (%)	SD (bar)	AD (%)	SD ($ml \cdot mol^{-1}$)	AD (%)
Ethane–H_2S	6	0.24	0.06	0.36	0.39	22.30	16.24
		0.29	0.07	0.35	0.26	16.00	11.45
		8.12	2.16	1.56	2.14	15.91	11.97
		5.91	1.49	7.48	9.57	4.29	2.68
Propane–H_2S	7	1.26	0.26	1.05	1.25	20.63	13.14
		1.49	0.32	1.65	2.32	19.76	12.28
		7.81	1.87	0.83	1.07	20.31	12.67
		19.90	4.45	18.60	23.90	6.35	3.64
Heptane–ethylene	8	2.00	0.4	7.04	7.74	27.60	7.41
		6.69	1.10	3.50	3.12	53.35	14.28
		9.71	1.80	5.09	5.95	56.77	15.99
		15.60	2.87	6.19	5.34	9.85	3.37
Methanol–1-butanol	4	0.27	0.03	5.01	6.00	55.10	27.27
		0.19	0.026	5.03	6.05	57.50	28.26
		1.04	0.16	5.15	6.16	57.43	28.22
		7.38	1.03	17.70	17.60	11.30	4.81
1-Butanol–diethyl ether	4	0.68	0.10	0.77	1.40	63.85	20.68
		0.73	0.11	0.81	1.52	56.37	18.41
		5.24	0.83	0.86	1.55	58.66	19.25
		1.18	0.13	1.05	1.82	13.90	3.27
SO_2–diethyl ether	4	0.41	0.06	2.77	4.17	35.35	15.42
		0.42	0.07	2.84	4.26	39.21	17.02
		4.44	0.83	3.15	4.55	38.59	16.79
		9.20	1.52	6.65	8.59	15.10	5.60
SO_2–methylethyl ether	5	0.96	0.17	0.43	0.62	37.06	19.19
		0.95	0.18	0.39	0.53	30.98	16.03
		9.41	1.88	1.30	1.71	30.90	16.00
		1.48	0.24	4.70	6.31	6.81	2.98
Average for all systems		0.83	0.24	2.49	3.08	37.41	17.05
		1.54	0.30	2.08	2.58	39.02	16.82
		6.54	1.36	2.56	3.30	37.80	17.27
		8.66	1.68	8.91	10.45	9.66	3.76

[a] First line: Margules two-parameter type (κ_{ij} listed in Table AIII). Second line: conventional one-parameter type (κ_{12} listed in Table AII). Third line: zero-parameter type ($\kappa_{12} = 0$). Fourth line: group-contribution method (Li and Kiran work).

On the other hand, the PRSV-2 predictive capability of the critical volumes is not as good as its predictive capability of the critical temperature and pressure. The group-contribution method [3] is superior in predicting the critical volume over the PRSV-2 and any other known cubic equation of state. The poor representation of the mixture critical volumes by cubic equations of state is well-known and has been widely attributed to the fact that the pure-component critical compressibility calculated from the equation of state is, in general, not equal to the experimental compressibility of most fluids [13]. The above statement is confirmed when one compares the pure-component critical compressibility predicted by the Peng–Robinson equation of state (0.3074) to the range of the experimental compressibilities of the pure compounds used in this study (0.224–0.290).

4. CONCLUSIONS

The PRSV-2 equation of state has been used in this work to predict the critical properties of binary mixtures on the basis of the algorithm adopted by Heidemann and Khalil [10]. The first and second partial derivatives of fugacity with respect to the mole numbers of the mixture constituents have been evaluated and the resulting two nonlinear equations have been solved simultaneously for the critical temperature and volume. The critical pressure is then calculated from the PRSV-2 equation of state itself. A quasi-Newton technique has been used here to calculate the optimum values of the binary interaction parameters that minimize the deviations between predicted and experimental critical temperatures. Zero-type, conventional one-parameter-type, and Margules two-parameter-type mixing rules have been tested.

The zero-parameter-type represents the actual predictive capability of the equation of state for the critical properties. The standard and the average of the absolute relative deviations in the critical temperature are always larger than those predicted using conventional one-parameter or Margules two-parameter types, even though these deviations using any of the three binary-interaction parameter types are comparatively similar.

Both conventional and Margules-type predictions of critical temperature and pressure agree well with the experimental data. The Margules type, in general, gives the best results, but its mathematical derivation is cumbersome and it requires more computation time. The deviations in the predicted critical volume, using any of the three tested binary-interaction parameter types, are relatively large. Better predictions are always obtained in both critical temperature and pressure compared to those obtained by the group-contribution method, which always gives lower deviations in the predicted critical volume.

APPENDIX A

Expressions for the First and Second Derivatives of the Fugacity of Component *m* with Respect to the Number of Moles of Species *l* and *k*

$$n_T\,\partial(\ln f_m)/\partial n_l$$

$$= C_1 - C_2 - C_3\{C_4/C_5 - C_6/C_5{}^2\} - C_7 + C_8 + C_9 + C_{10}C_{15}\{C_{11} + C_{12} - C_{13} - C_{14}\} + C_{10}(C_{16} - C_{17})(C_{18} - C_{19})$$

where

$$C_1 = b_m v/b(v-b),$$

$$C_2 = b_m b_l v(v-2b)/[b(v-b)]^2$$

$$C_3 = b_m v/RT$$

$$C_4 = \sum_j^N x_j(a_{ji} + a_{ij})$$

$$C_5 = b(v^2 + 2vb - b^2)$$

$$C_6 = ab_l(v^2 + 4vb - 3b^2)$$

$$C_7 = b_m/b - b_m b_l/b^2$$

$$C_8 = \delta_{m1}/x_m, \qquad \delta = 1.0 \text{ for } m = 1,\ \delta = 0 \text{ for } m \neq 1$$

$$C_9 = b_l/(v-b)$$

$$C_{10} = \tfrac{1}{2}\sqrt{2}\,RT$$

$$C_{11} = C_4 b_m/b^2$$

$$C_{12} = b_l \sum_j^N x_j(a_{jm} + a_{mj})/b^2$$

$$C_{13} = 2ab_m b_l/b^3$$

$$C_{14} = (a_{lm} + a_{ml})/b$$

$$C_{15} = \ln\{(v + (1+\sqrt{2})\,b)/(v + (1-\sqrt{2})\,b)\}$$

$$C_{16} = aC_{10} b_m / b^2$$

$$C_{17} = C_{10} \sum_j^N x_j (a_{mj} + a_{jm}) / b$$

$$C_{18} = (1 + \sqrt{2})\, b_l / (v + (1 + \sqrt{2})\, b)$$

$$C_{19} = (1 - \sqrt{2})\, b_l / (v + (1 - \sqrt{2})\, b)$$

$$\begin{aligned} n_T{}^2\, \partial^2 (\ln f_m) / \partial n_l\, \partial n_k \\ &= [\, -D_1 - D_2 + D_3 - D_4 + D_6 + D_9 - D_{10} + D_{11} + D_{12} - D_{13} + D_{14}] \\ &\quad + C_{10} C_{15} \{D_{15} - D_{16} + D_{17} - D_{18} - D_{20} + D_{21} + D_{22}\} \\ &\quad + D_{23} \{D_{24} + D_{25} - D_{26} - D_{27}\} + D_{28} \{D_{29} - D_{30} - D_{31} + D_{32}\} \\ &\quad + D_{33} \{D_{34} - D_{35}\} \end{aligned}$$

where

$$D_1 = b_m b_k v (v - 2b) / [b(v - b)]^2$$

$$D_2 = b_m b_l v (v - 2b - 2b_k) / [b(v - b)]^2$$

$$D_3 = 2 b_m b_l b_k v (v - 2b)^2 / [b(v - b)]^3$$

$$D_4 = b_m v (a_{kl} + a_{lk}) / (RTC_5)$$

$$D_5 = v^2 + 4bv - 3b^2$$

$$D_6 = b_m b_k v C_4 D_5 / [RTC_5{}^2]$$

$$D_7 = v D_5 \sum_j^N x_j (a_{jk} + a_{kj})$$

$$D_8 = a b_k v (4v - 6b)$$

$$D_9 = b_m b_l (D_7 + D_8) / [RTC_5{}^2]$$

$$D_{10} = 2 a b_m b_l b_k v (D_5{}^2) / [RTC_5{}^3]$$

$$D_{11} = b_m b_k / b^2$$

$$D_{12} = b_m b_l / b^2 - 2 b_m b_l b_k / b^3$$

$$D_{13} = \delta_{mlk} / x_m{}^2$$

where $\delta = 1.0$ for $m = l = k$, and $\delta = 0$ for $m \neq l \neq k$.

$$D_{14} = b_l b_k/(v-b)^2$$

$$D_{15} = b_m(a_{kl} + a_{lk})/b^2$$

$$D_{16} = 2b_m b_k \sum_j^N x_j(a_{jl} + a_{lj})/b^3$$

$$D_{17} = b_l(a_{mk} + a_{km})/b^2$$

$$D_{18} = 2b_l b_k \sum_j^N x_j(a_{jm} + a_{mj})/b^3$$

$$D_{20} = 2b_m b_l \sum_j^N x_j(a_{jk} + a_{kj})/b^3$$

$$D_{21} = 6ab_m b_l b_k/b^4$$

$$D_{22} = b_k(a_{ml} + a_{lm})/b^2$$

$$D_{23} = C_{10}(C_{18} - C_{19})\, b_k/b_l$$

$$D_{24} = b_m \sum_j^N x_j(a_{jl} + a_{lj})/b^2$$

$$D_{25} = b_l \sum_j^N x_j(a_{jm} + a_{mj})/b^2$$

$$D_{26} = 2ab_m b_l/b^3$$

$$D_{27} = (a_{lm} + a_{ml})/b$$

$$D_{28} = C_{10}(C_{18} - C_{19})$$

$$D_{29} = b_m \sum_j^N x_j(a_{jk} + a_{kj})/b^2$$

$$D_{30} = 2ab_m b_k/b^3$$

$$D_{31} = (a_{mk} + a_{km})/b$$

$$D_{32} = b_k \sum_j^N x_j(a_{jm} + a_{mj})/b^2$$

$$D_{33} = C_{10}(C_{19}{}^2 - C_{18}{}^2)\, b_k/b_l$$

$$D_{34} = ab_m/b^2$$

$$D_{35} = \sum_j^N x_j(a_{jm} + a_{mj})/b$$

APPENDIX B

Table AI. Pure-Component Properties

Compound	T_c (K)	P_c (kPa)	ω	κ_1	κ_2	κ_3
NH_3	405.6	11289.5	0.2517	0.001	−0.1265	0.51
SO_2	430.8	7883.1	0.251	0.03962	NA	NA
HCl	324.6	8308.6	0.12606	0.01989	−0.0036	0.31
H_2S	373.2	8940.0	0.1	0.03160	NA	NA
N_2	126.2	3400.0	0.03726	0.01996	0.3162	0.535
O_2	154.8	5090.0	0.02128	0.01512	−0.009	0.49
H_2O	647.3	22089.8	0.3438	−0.06635	0.0199	0.443
Methane	190.6	4595.0	0.01045	−0.00159	0.1521	0.517
Ethane	305.4	4879.8	0.09781	0.02669	0.1358	0.424
Propane	369.8	4249.5	0.15416	0.03136	0.2757	0.447
Butane	425.2	3796.6	0.20096	0.03443	0.6767	0.461
Hexane	507.3	3012.4	0.30075	0.05104	0.8634	0.460
Heptane	540.1	2735.8	0.35022	0.04648	0.9331	0.496
Nonane	594.6	2287.9	0.44517	0.04104	0.6621	0.519
Decane	617.5	2103.5	0.49052	0.04510	0.8549	0.527
Ethylene	282.4	5035.9	0.085	0.04191	NA	NA
Cyclohexane	553.6	4075.0	0.20877	0.07023	0.6146	0.530
Benzene	562.2	4898.0	0.20929	0.07019	0.7939	0.523
Toluene	591.8	4106.0	0.26323	0.03849	0.5261	0.510
Methanol	512.6	8095.8	0.56533	−0.16816	−1.34	0.588
Ethanol	513.9	6148.0	0.64439	−0.03374	−2.6846	0.592
1-Butanol	563.0	4412.7	0.5902	0.33431	−1.17431	0.642
Acetone	508.1	4696.0	0.30667	−0.00888	0.2871	0.537
Diethyl ether	466.7	3640.0	0.281	0.05004	NA	NA
Methylethyl ether	437.8	4410.0	0.23479	0.16948	0.0515	0.768
Hexafluorobenzene	516.7	3273.0	0.3961	0.02752	0.8172	0.565

Table AII. Optimized Values of the Conventional Binary Interaction Parameter, κ_{12}

Mixture	κ_{12}
Methane–ethane	0.03161
Ethane–butane	0.02911
Ethane–heptane	0.08192
Ethane–H_2S	0.09365
Butane–ammonia	0.15633
Butane–heptane	0.03413
Propane–H_2S	0.07710
Propane–HCl	0.07383
Hexane–heptane	0.00135
Hexane–decane	0.02080
Hexane–cyclohexane	−0.01629
Heptane–ethylene	0.06484
Nonane–cyclohexane	−0.02777
Nitrogen–oxygen	−0.02115
Acetone–benzene	0.01073
Benzene–methanol	0.07671
Benzene–toluene	−0.00752
Methanol–1-butanol	−0.00900
Ethanol–water	−0.05187
1-Butanol–diethyl ether	0.04865
Hexafluorobenzene–decane	0.08790
SO_2–diethyl ether	−0.03832
SO_2–methylethyl ether	−0.08064

Table AIII. Optimized Values of the Margules Two-Binary Interaction Parameters

Mixture	κ_{12}	κ_{21}
Ethane–H_2S	0.098847	0.086689
Propane–H_2S	−0.027775	0.100737
Butane–CO_2	0.105994	0.026026
Heptane–ethylene	−0.127265	−0.066530
Methanol–1-butanol	−0.010793	−0.009189
1-Butanol–diethyl ether	0.054538	0.044945
SO_2–diethyl ether	−0.038200	−0.041420
SO_2–methylethyl ether	−0.081787	−0.084040

NOMENCLATURE

a	Attraction parameter in the Peng–Robinson equation of state
A	$aP/(RT)^2$
A	Helmholtz free energy
AD	Average of the absolute relative deviations defined by Eq. (22)
b	Repulsion parameter in the Peng–Robinson equation of state
B	bP/RT
C	Cubic term defined in Eq. (20)
C'	Derivative of the cubic term C
Det	Determinant
f	Fugacity
k	Binary interaction parameter
M	Number of data points
n	Number of moles
N	Number of components
P	Pressure (bar)
Q	Matrix in the quadratic terms defined in Eq. (14)
Q'	Derivative of the Q matrix
q	Elements of the Q matrix defined by Eq. (18)
R	Universal gas constant
SD	Standard deviation defined by Eq. (21)
T	Absolute temperature (K)
V	Volume (ml)
v	Molar volume ($\mathrm{ml \cdot mol^{-1}}$)
x	Mole fraction
Z	Compressibility factor

Greek Letters

Δ	Difference in property
ε	Error tolerance
κ	Function of reduced temperature and acentric factor, Eq. (5)
κ_0	Function of acentric factor, Eq. (6)
$\kappa_1, \kappa_2, \kappa_3$	Pure compound parameters in the PRSV-2 equation of state
ω	Acentric factor

Subscripts

c	Critical property
i, j, k, l, m, n	Component number

m	Mixture property
0	Initial state
r	Reduced property
T	Total property

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