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Prediction of multicomponent vapor–liquid equilibria using the PRSV and PRSV2 equations of state with the Huron–Vidal mixing rules

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Abstract

The Stryjek–Vera modifications of the Peng–Robinson equation of state are tested for the prediction of multicomponent vapor–liquid equilibria at low pressures for highly non-ideal systems including seven ternary, two quaternary and one quinary mixtures. The Huron–Vidal mixing rules from three excess free energy models are used for the calculation of the parameters in the PRSV and PRSV2 equations of state. The two equations of state with the mixing rules perform equally well.

INTRODUCTION

Recently, much attention has been given to the calculations of vapor–liquid and liquid–liquid equilibria (VLE and LLE), in which the same equation of state with a pertinent mixing rule is used to represent coexisting phases. The good capabilities of the PRSV2 equation of state with the NRTL mixing rule in predicting ternary phase equilibria at low and high pressures have been shown for a variety of mixtures [1,2]. The predictions of ternary low-pressure VLE have been carried out to test the abilities of the PRSV and PRSV2 equations of state coupled with several mixing rules [3,4].

In this work, the prediction accuracy of the PRSV and PRSV2 equations with the Huron–Vidal mixing rules obtained from the NRTL, modified UNIQUAC, and only residual part of UNIQUAC models is shown for various kinds of non-ideal multicomponent mixtures, including seven ternary, two quaternary, and one quinary systems.

THE PRSV AND PRSV2 EQUATIONS OF STATE

The PRSV and PRSV2 equations of state [5,6] are basically similar to the Peng–Robinson equation [7], namely

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

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where

$$a = \left(0.457235 R^2 T_c^2 / P_c\right) \alpha \tag{2}$$

$$b = 0.077796 R T_c / P_c \tag{3}$$

and

$$\alpha = \left[1 + \kappa\left(1 - T_{\mathrm{R}}^{0.5}\right)\right]^2 \tag{4}$$

In the PRSV equation, the κ term is expressed by

$$\kappa = \kappa_0 + \kappa_1\left(1 + T_{\mathrm{R}}^{0.5}\right)(0.7 - T_{\mathrm{R}}) \tag{5a}$$

Furthermore, Stryjek and Vera have proposed an extended form, called the PRSV2

$$\kappa = \kappa_0 + \left[\kappa_1 + \kappa_2(\kappa_3 - T_{\mathrm{R}})\left(1 - T_{\mathrm{R}}^{0.5}\right)\right]\left(1 + T_{\mathrm{R}}^{0.5}\right)(0.7 - T_{\mathrm{R}}) \tag{5b}$$

If $\kappa_2 = 0$, eqn. (5b) reduces to the PRSV form. In both expressions, eqns. (5a) and (5b), κ_0 is given by

$$\kappa_0 = 0.378893 + 1.4897153\omega - 0.17131848\omega^2 + 0.0196554\omega^3 \tag{6}$$

The values of pure component parameters κ_1, κ_2, and κ_3 are available in the papers of Stryjek and Vera [5,6] and Proust and Vera [8], together with those of critical constants and acentric factor.

THE HURON–VIDAL MIXING RULE

Huron and Vidal [9] developed the following mixing rule for mixtures using the excess Gibbs energy at infinite pressure

$$a = b\left(\sum_i x_i \frac{a_{ii}}{b_i} - c g_\infty^{\mathrm{E}}\right) \tag{7}$$

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

where c is the numerical constant equal to $2\sqrt{2}/\ln[(2+\sqrt{2})/(2-\sqrt{2})]$ for the present equations of state.

For excess free energy at infinite pressure g_∞^{E}, the three different models based on the local composition concept were investigated as follows.

I. NRTL model [10]

$$g_\infty^{\mathrm{E}}/RT = \sum_i x_i \frac{\sum_j \tau_{ji} G_{ji} x_j}{\sum_k G_{ki} x_k} \tag{9}$$

with

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \tag{10}$$

$$\tau_{ij} = a_{ij}/T \tag{11}$$

where α_{ij} ($\alpha_{ij} = \alpha_{ji}$) is a non-randomness constant. The values of α_{ij} were taken from a previous paper [1].

II. UNIQUAC model [11]

$$g^{\mathrm{E}}_{\infty}/RT = \sum_i x_i \ln(\phi_i/x_i) + \left(\frac{Z}{2}\right)\sum_i q_i x_i \ln(\theta_i/\phi_i) - \sum_i q_i' x_i \ln\left(\sum_j \theta_j' \tau_{ji}\right) \tag{12}$$

with

$$\phi_i = r_i x_i / \sum_j (r_j x_j) \tag{13}$$

$$\theta_i = q_i x_i / \sum_j (q_j x_j) \tag{14}$$

$$\theta_i' = q_i' x_i / \sum_j (q_j' x_j) \tag{15}$$

$$\tau_{ij} = \exp(-a_{ij}/T) \tag{16}$$

where Z is the coordination number and equal to 10. The pure component structural parameters r, q and q' were given in the monograph of Prausnitz et al. [12].

III. Residual part of UNIQUAC model [13]

$$g^{\mathrm{E}}_{\infty}/RT = -\sum_i q_i x_i \ln\left(\sum_j \theta_j \tau_{ji}\right) \tag{17}$$

with

$$\theta_i = q_i x_i / \sum_j (q_j x_j) \tag{18}$$

$$\tau_{ij} = \exp(-a_{ij}/T) \tag{19}$$

where the pure area parameter q is the same as that of the above UNIQUAC model.

It has been shown that the combination of the PRSV2 equation of state with the NRTL model yields good results for non-ideal binary and ternary mixtures [1]. The modified UNIQUAC model of Anderson and Prausnitz

TABLE 1

Binary parameters

System (1–2)	Temp. (°C)	No. of data points	Model	Energy parameters (K)				α_{12}	Variance of fit		Ref.
				PRSV		PRSV2			PRSV	PRSV2	
				a_{12}	a_{21}	a_{12}	a_{21}				
Water–methanol	25	10	I [a]	207.89	79.92	279.00	20.70	0.30	9.49	4.98	19
			II [b]	144.26	−21.27	135.95	−15.21		4.37	4.84	
			III [c]	173.87	35.58	169.63	39.67		5.57	6.48	
Water–ethanol	25	10	I	568.23	181.82	549.06	156.17	0.30	14.91	42.61	19
			II	329.47	188.58	481.53	102.50		32.44	15.88	
			III	296.66	121.49	326.80	126.88		35.58	24.12	
Methanol–ethanol	25	11	I	59.35	−48.99	−97.66	118.56	0.30	5.65	5.68	19
			II	26.29	−1.58	40.75	−21.99		5.42	6.78	
			III	137.58	−113.95	52.08	−43.78		7.79	5.69	
Ethanol–methanol	40	13	I	−85.98	94.99	−124.69	151.60	0.30	0.08	0.02	20
			II	−77.40	112.83	−87.71	135.92		0.06	0.01	
			III	−70.19	80.08	−80.01	98.10		0.08	0.01	
Ethanol–2-butanone	25	12	I	175.56	186.29	165.92	194.67	0.30	3.96	3.49	21
			II	−124.25	542.19	−128.61	563.81		3.54	3.26	
			III	−22.96	187.27	−30.36	200.07		3.74	3.58	
Ethanol–benzene	25	11	I	213.29	714.99	210.35	717.78	0.35	12.83	12.66	21
			II	−84.06	2233.77	−84.23	1882.77		2.39	2.50	
			III	−32.32	489.00	−27.22	473.97		15.84	15.06	
	45	12	I	231.32	686.31	235.81	674.22	0.35	7.20	7.73	22
			II	−89.04	1203.01	−87.45	1169.30		5.90	5.87	
			III	−16.23	453.56	−12.92	444.67		9.91	10.86	

Benzene–2-butanone	25	10	I	399.84	−227.26	352.92	−201.36	0.30	3.50	4.48	21
			II	273.85	−179.05	242.75	−164.37		2.76	3.75	
			III	193.76	−123.28	167.74	−107.40		3.19	4.14	
Chloroform–methanol	50	25	I	735.73	64.01			0.35	2.36		23
			II	1153.48	−114.24				13.46		
			III	732.13	−117.61				3.63		
Acetone–methanol	50	16	I	120.47	190.07			0.30	0.02		23
			II	433.30	−87.67				0.05		
			III	240.49	−41.91				0.02		
Acetone–chloroform	50	15	I	−278.52	21.68			0.30	2.63		23
			II	−142.10	31.45				2.75		
			III	−142.78	34.31				2.75		
Methyl acetate–chloroform	50	16	I	−402.47	217.33			0.30	3.05		24
			II	−185.47	101.14				3.25		
			III	−190.20	111.97				3.33		
Methyl acetate–benzene	50	17	I	140.41	−3.96			0.30	7.68		24
			II	108.72	−76.34				7.64		
			III	111.00	−48.63				7.35		
Chloroform–benzene	50	19	I	36.56	−113.04			0.30	2.77		24
			II	17.79	−63.60				2.75		
			III	29.13	−60.61				2.75		
Methanol–acetonitrile	55	13	I	267.26	201.27	277.00	198.25	0.30	2.82	4.42	25
			II	23.02	420.14	28.82	417.01		2.19	3.36	
			III	104.67	199.17	110.65	196.80		2.59	4.14	

TABLE 1 (continued)

System (1–2)	Temp. (°C)	No. of data points	Model	Energy parameters (K)				α_{12}	Variance of fit		Ref.
				PRSV		PRSV2			PRSV	PRSV2	
				a_{12}	a_{21}	a_{12}	a_{21}				
Methanol–benzene	55	9	I	452.00	715.54	453.36	710.65	0.35	10.42	10.68	26
			II	20.46	1218.95	21.84	1201.36		22.62	21.19	
			III	34.11	674.30	35.14	669.66		11.52	12.48	
Ethanol–acetonitrile	40	14	I	300.01	231.59	298.70	237.33	0.30	4.79	6.46	27
			II	47.80	476.86	50.27	479.37		3.51	4.79	
			III	214.64	76.69	213.80	79.53		4.75	6.38	
Acetonitrile–benzene	45	12	I	188.51	220.43	207.35	198.79	0.30	3.79	3.22	28
			II	−25.80	239.81	−16.84	224.84		3.44	2.96	
			III	−10.75	230.77	−1.21	215.59		3.74	3.19	
1-Propanol–ethanol	40	10	I	380.73	−251.65	−80.17	100.90	0.30	0.07	0.01	20
			II	287.99	−159.45	74.39	−42.02		0.07	0.02	
			III	245.52	−165.15	70.60	−57.95		0.07	0.01	
Acetonitrile–1-propanol	55	10	I	212.51	316.44	216.94	311.44	0.30	11.69	7.85	29
			II	524.93	45.70	531.12	42.60		9.70	5.61	
			III	−19.96	306.52	−16.74	300.70		11.61	7.66	
1-Propanol–benzene	45	11	I	135.75	638.48	129.08	626.76	0.35	6.92	2.72	30
			II	−139.60	1137.08	−142.41	1097.32		3.01	0.48	
			III	−16.97	317.89	−15.35	308.00		8.25	3.65	

[a] I = NRTL model.

[b] II = Modified UNIQUAC model.

[c] III = Residual part of UNIQUAC model.

[11], which has different values for the pure component area parameter q for water and alcohols in the combinatorial and residual parts, gives satisfactory results for various systems containing these components in VLE data analysis with the γ–ψ method. As discussed by several investigators [14–17], a Flory combinatorial term already exists in an equation of state. Therefore, the third model selected was that of only the residual UNIQUAC contribution.

VAPOR-LIQUID EQUILIBRIUM CALCULATIONS

The vapor–liquid equilibrium relationship for any component i is written in terms of fugacity coefficients

$$\psi_i^V y_i = \psi_i^L x_i \tag{20}$$

where x_i and y_i are the liquid and vapor mole fractions of component i. The fugacity coefficients for both the phases are thermodynamically derived from the equation of state.

A computer program used for binary parameter estimation was based on the maximum likelihood principle as described by Anderson and Prausnitz [18]. Standard deviations in the measured variables were used as: $\sigma_P = 1.0$ Torr, $\sigma_T = 0.05$ K, $\sigma_x = 0.001$, $\sigma_y = 0.003$.

Predictions of multicomponent VLE data from binary data were done by using the bubble-point pressure calculation shown by Anderson and Prausnitz [18].

RESULTS

Table 1 lists the binary parameters obtained in binary VLE data reduction, together with the estimated variance of the fit. The three models for excess free energy at infinite pressure can reproduce binary data well. The parameters were used to predict multicomponent VLE data for the systems studied here.

Table 2 summarizes VLE predictions for the multicomponent systems. The predictions from binary data alone are considered good. The predicted results from the PRSV and PRSV2 equations of state indicate that both equations have similar predictive ability. This means that the use of the PRSV2 equation does not give large improvements in prediction of multicomponent VLE data.

Of the three models selected for expression of excess Gibbs energy at infinite pressure in the Huron–Vidal mixing rule, the NRTL and the only residual part of UNIQUAC models produce slightly better results in vapor mole fraction than the full UNIQUAC model for most of the systems, and the residual part gives the best prediction in equilibrium pressure for the

TABLE 2

Deviations of predicted values from experimental data for multicomponent systems

System	Temp. or press.	Number of data points	Absolute arithmetic mean deviations												Ref.
			Vapor mole fraction (×1000)						Pressure (Torr)						
			PRSV			PRSV2			PRSV			PRSV2			
			I [a]	II [b]	III [c]	I	II	III	I	II	III	I	II	III	
Ternaries															
Water–	25 °C	37	5.1	4.9	4.0	6.5	3.8	3.0	1.3	0.8	0.7	1.0	0.7	1.2	19
methanol–			3.2	4.5	6.9	6.6	3.3	4.4							
ethanol			3.0	5.3	6.1	6.4	3.0	2.9							
Ethanol–	25 °C	33	4.5	4.7	4.5	4.6	4.2	4.3	1.7	1.7	1.9	1.6	1.3	1.6	21
2-butanone–			3.0	3.0	3.1	3.3	3.2	3.6							
benzene			4.6	5.7	4.9	5.3	5.0	5.0							
Methanol–	50 °C	42	7.5	5.1	7.8				6.4	4.8	7.1				23
chloroform–			7.5	5.8	7.8										
acetone			4.3	3.4	4.5										
Methyl acetate–	50 °C	66	4.6	4.2	4.5				2.5	2.5	2.5				24
chloroform–			2.8	2.8	3.0										
benzene			3.7	3.1	3.5										
Acetonitrile–	55 °C	17	5.1	6.3	5.0	5.6	6.6	5.4	4.4	3.6	4.3	4.2	3.4	4.2	31
methanol–			6.8	8.2	7.0	7.5	8.6	7.5							
benzene			3.7	5.0	3.9	4.0	5.2	4.2							

Ethanol–	45 ° C	21	7.1	7.3	4.0	7.3	7.7	6.4	1.3	4.0	1.1	1.3	3.8	1.2	32
acetonitrile–			5.0	7.3	6.2	5.2	7.5	4.1							
benzene			3.7	4.9	3.8	3.9	5.3	3.8							
1-Propanol–	45 ° C	27	5.4	6.9	5.7	3.4	5.3	3.7	2.0	4.9	1.6	2.1	5.1	1.6	33
acetonitrile–			6.3	9.3	5.0	6.1	9.3	4.6							
benzene			8.2	11.8	7.5	7.2	10.8	6.5							
Quaternaries															
Methanol–	45 ° C	25	3.4	4.1	3.5	3.8	4.4	3.6	5.3	8.6	2.7	5.7	9.2	2.8	34
ethanol–			8.0	8.5	7.0	8.7	9.6	7.4							
acetonitrile–			5.3	5.8	4.7	5.3	6.0	4.7							
benzene			7.8	11.6	6.5	8.2	12.1	6.4							
Ethanol–	45 ° C	24	5.2	4.9	5.4	4.3	5.4	4.1	2.6	5.8	2.0	3.0	6.0	2.1	35
1-propanol–			5.1	6.6	4.9	4.4	5.7	3.9							
acetonitrile–			4.5	5.2	3.8	5.0	5.4	4.1							
benzene			4.0	9.6	3.7	3.4	8.9	3.3							
Quinary															
Benzene–	760 Torr	15	3.4	3.9	3.6				9.5	11.3	11.8				36
chloroform–			3.2	3.8	3.8										
methanol–			14.6	12.8	14.4										
methyl acetate–			5.7	4.0	5.1										
acetone			7.5	6.2	6.4										

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[a] I = NRTL model.

[b] II = Modified UNIQUAC model.

[c] III = Residual part of UNIQUAC model.

quaternary systems. The prediction accuracy of the present approach seems to be comparable with that of the γ–ψ approach.

In conclusion, the PRSV and PRSV2 equations of state coupled with the Huron–Vidal mixing rules from the local composition equations perform well in the prediction of multicomponent VLE for highly non-ideal mixtures.

LIST OF SYMBOLS

a	parameter of the equations of state
a_{ij}	binary interaction parameter
b	parameter of the equations of state
c	numerical constant
g^{E}_{∞}	excess Gibbs energy at infinite pressure
P	total pressure
q	molecular-geometric area parameter
q'	molecular-interaction area parameter
R	gas constant
r	molecular volume parameter
T	absolute temperature
v	molar volume
x	mole fraction
y	vapor mole fraction
Z	coordination number, equal to 10

Greek letters

α	function of reduced temperature and acentric factor
α_{ij}	non-randomness parameter
γ	activity coefficient
θ	area fraction
σ_P, σ_T, σ_x, σ_y	standard deviations in pressure, temperature, liquid mole fraction, and vapor mole fraction
τ	binary parameter
ψ	fugacity coefficient
ϕ	volume fraction
ω	acentric factor
κ	function of reduced temperature and acentric factor
κ_0	function of acentric factor
κ_1, κ_2, κ_3	pure component parameters

Subscripts

c	critical property
i, j	components
R	reduced temperature
∞	at infinite pressure

Superscripts

E	excess property
L	liquid phase
V	vapor phase

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