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Prediction of vapor–liquid equilibria of binary systems using PRSV equation of state and Wong–Sandler mixing rules

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Abstract

The Peng–Robinson equation of state modified by Stryjek and Vera (1986) has been used with Wong–Sandler mixing rules (1992) to predict vapor–liquid equilibria of forty-three binary mixtures involving organic alcohols, esters, ketones, amines, etc. The Wong–Sandler mixing rules are theoretically correct in the sense that they reproduce quadratic composition dependence of the second virial coefficient. However, recent studies indicate that the basic premises of these rules break down for highly asymmetric systems and at high pressures. The systems studied have low to moderate asymmetry. It has been observed that the non random two liquid (NRTL) model provides a good representation of G^E models and the results obtained from optimization compare well with those reported in DECHEMA data series in spite of the asymmetry inherent to these systems. The results obtained from this study can be used directly to predict vapor–liquid equilibria involving such systems.

Keywords: Theory; Application; Optimization; Cubic equation of state; Mixing rules; Excess functions

1. Introduction

Cubic equations of state are widely in use to predict vapor–liquid equilibria (VLE) of fluid mixtures due to their algebraic simplicity and often high accuracy. However, the main difficultly in describing the phase behavior for a broad range of multicomponent mixtures at various temperatures and pressures was the nonavailability of proper mixing rules and combining rules. The van der Waals one fluid mixing rules and combining rules are adequate to describe the phase behavior of a wide variety of multicomponent mixtures—the so called 'ideal mixtures'. To model complex phase behavior of highly nonideal mixtures, several efforts were made [1–3].

These mixing rules have been found to be satisfactory in predicting the phase behavior of complex binary mixtures, including extremely non-ideal systems. But in the low-density limit, these modified mixing rules are inconsistent with the statistical mechanical result that the second viral coefficient is a quadratic function of composition. Some work has been done in this direction to develop density dependent mixing rules [4–6]. An alternative approach has been made by Vidal [7] and later on by Huron and Vidal [8] by equating the excess Gibbs free energy at infinite pressure calculated from an equation of state to that obtained from an activity coefficient model for liquids. But the Huron–Vidal mixing rule has two serious drawbacks. The first shortcoming is that the mixing rule is based on the assumption that the excess Gibbs free energy is independent of pressure, which is not true. Secondly, the mixing rule does not satisfy the requirement that the second virial coefficient is a quadratic function of composition. Several attempts have been made to relax the infinite-pressure limit imposed on the Huron–Vidal model [9–13]. In all cases, it has been postulated that the covolume parameter 'b' is linearly related to composition, i.e., $b_m = \Sigma x_i b_i$, where x_i represents the mixture composition. These purely predictive zero reference pressure (ZRP) models do give good results in many binary systems and even for several complex mixtures. But these models do not predict the VLE correctly as the system asymmetry increases (A binary system is called asymmetric, when the ratio of covolume parameters of its pure constituents ($\equiv b_1/b_2$) deviates from unity. The more it deviates, the more asymmetric the system is). As a consequence, these models fail to predict the behavior of systems involving light gases (like methane, ethane, etc.) and n-alkanes.

In 1992, Wong and Sandler [14] developed a new class of mixing rules that correctly represents the quadratic com-

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position dependence of the second virial coefficient and in addition, retains the ability to predict high pressure–high temperature phase equilibria from existing low pressure G^E models directly. Several works have followed [15–18] which demonstrated the applicability and limitations of these Wong–Sandler mixing rules (WSMR).

In this work we have used the Peng–Robinson equation of state modified by Stryjek and Vera (PRSV) [19,20] along with the Wong–Sandler mixing rules to predict vapor–liquid equilibria of forty three binary mixtures involving organic oxygenated and nitrogenated compounds like alcohols, esters, amines, aldehydes, ketones, etc. These mixtures have various degrees of asymmetry ranging from low to moderate ($0.4 < b_1/b_2 < 1.6$). Our objective is to test the performance of PRSV–WSMR combination in predicting the VLE for such systems, and at the same time evaluate the necessary parameters for direct use by optimizing them with available experimental VLE data at different temperatures. Also, we aim to investigate the effect of low to moderate asymmetry at low pressures on these mixing rules. We have used the NRTL (non random two liquid) model of Renon and Prausnitz [21] exclusively as the G^E model. The PRSV equation of state, the Wong–Sandler mixing rules and the NRTL model are discussed in Section 2.

2. The PRSV equation of state

The original Peng–Robinson equation of state [22] provided accurate vapor pressure predictions or hydrocarbons in the 6–10 carbon number range (i.e., gasoline fractions). The equation of state is

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

where,

$$a = (0.457235 R^2 T_c^2 / P_c)\alpha \qquad (2)$$

and

$$b = 0.077796 RT_c / P_c \qquad (3)$$

Soave used the following correlation for α,

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

where, κ was considered to be a function of the acentric factor ω only. Stryjek and Vera [19,20] modified the functional dependence of the κ parameter. A major improvement in the prediction capability was achieved with the following simple expression for κ

$$\kappa = \kappa_0 + \kappa_1(1 + T_R^{0.5})(0.7 - T_R) \qquad (5)$$

where,

$$\kappa_0 = 0.378893 + 1.4897153\omega - 0.17131848\omega^2 + 0.0196554\omega^3 \qquad (6)$$

κ_1 is a characteristic parameter of the pure component. In view of the empirical nature of κ_1, no correlation has been found for it in terms of the pure component properties. κ_1 values are calculated from the experimental vapor pressure data when the T_c, P_c and ω values of the pure component concerned are known. The κ_1 values for a wide variety of pure compounds are available in Ref. [19].

3. The Wong–Sandler mixing rules

Wong and Sandler [14] developed a set of theoretically correct mixing rules based on two major observations. The first one is, while the van der Waals one fluid mixing rules for both 'a' and 'b' parameters are sufficient conditions to insure the proper composition dependence of the second virial coefficient, they are not the necessary conditions. In fact, the van der Waals one fluid mixing rule is one of the solutions of the following relation obtained from statistical mechanics

$$B_m = \sum_i \sum_j x_i x_j B_{ij}(T) = \sum_i \sum_j x_i x_j \left(b - \frac{a}{RT}\right)_{ij} = b_m - \frac{a_m}{RT} \qquad (7)$$

When coupled with the combining rule,

$$\left(b - \frac{a}{RT}\right)_{ij} = \frac{\left(b_i - \frac{a_i}{RT}\right) + \left(b_j - \frac{a_j}{RT}\right)}{2}(1 - k_{ij}) \qquad (8)$$

it introduces a second virial coefficient binary interaction parameter, k_{ij}. Other solutions for a_m and b_m which are also possible can be obtained from the second observation.

The second observation is, the excess Helmholtz free energy of a mixture is much less pressure dependent than the excess Gibbs free energy, i.e.,

$$G^E(T, P = \text{low}, x_i) = A^E(T, P = \text{low}, x_i) = A^E(T, P = \infty, x_i) \qquad (9)$$

The first of these equalities follow from the fact that $G^E = A^E + Pv^E$, and the Pv^E term is very small at low pressures. The second of these equalities is a result of the essential pressure independence of A^E. The second equation for a_m and b_m then comes from the condition that

$$A^E_{\text{EoS}}(T, P = \infty, x_i) = A^E(T, P = \infty, x_i) = A^E(T, \text{low}P, x_i) \qquad (10)$$

where A^E_{EoS} refers to the excess Helmholtz free energy derived from an equation of state, while the quantities A^E and G^E indicate excess free energies derived from an activity coefficient model.

The infinite pressure limit of an equation of state corresponds to the assumption that in the liquid solution the molecules are so closely packed that there is no free volume

$$\lim_{P \to \infty} v = b$$

On the other hand, expressions for A^E of liquid solutions have usually been derived using lattice models with the assumption that there are no free sites on the lattice. These assumptions seem to be approximately equivalent, and, consequently, information from a liquid solution model can be incorporated into an equation of state by taking the infinite pressure limit in the excess Helmholtz free energy functions.

From the above set of equations, Wong and Sandler [14] obtained the following expressions for a_m and b_m as

$$b_m = \frac{\sum_i \sum_j x_i x_j \left(b - \frac{a}{RT}\right)_{ij}}{1 - \frac{A^E_\infty}{CRT} - \sum_i x_i \frac{a_i}{RTb_i}} \qquad (11)$$

and

$$a_m = b_m \left[\sum_i x_i \frac{a_i}{b_i} + \frac{A^E_\infty}{C}\right] \qquad (12)$$

Here, C is an equation of state dependent constant which is $\ln(\sqrt{2}-1)/\sqrt{2}$ for the PRSV equation of state. The expression for A^E_∞ for NRTL model is

$$\frac{A^E_\infty}{RT} = \sum_i x_i \left[\frac{\sum_j x_j \tau_{ji} g_{ji}}{\sum_k x_k g_{ki}}\right] \qquad (13)$$

A detailed derivation has been given by Wong and Sandler [14]. Further, in order to make the model more predictive, Orbey et al. [17] estimated the value of k_{ij} by solving the equation

$$\left(\frac{G^E}{RT}\right)^{\text{EoS}} = \left(\frac{G^E(x)}{RT}\right)^{\text{solution model}} \qquad (14)$$

at a specific composition of each binary mixture ($x_i = 0.5$) and at low temperature (298 K) and pressure; k_{ij} can also be calculated using VLE data throughout the composition range.

In a recent paper, Coutsikos et al. [23] have shown that the binary interaction parameter really depends on composition. This dependence on composition increases as the system asymmetry increases. In the extreme situations, composition dependence of k_{ij} leads to the violation of quadratic composition dependence of the second virial coefficient. Also, in those cases, k_{ij} assume values greater than unity, which is physically unrealistic. These authors have also indicated that, as the system asymmetry increases, at high pressures, the basic premises of these rules break down, i.e., increase in system asymmetry leads to

$$G^E(T, P = \text{low}, x_i) = A^E(T, P = \text{low}, x_i) \neq A^E(T, P = \infty, x_i) \qquad (15)$$

Similar results on the effect of high pressure on these mixing rules are also available in literature [24].

Orbey and Sandler [18] recently reformulated the mixing rule to eliminate one of its parameters so that it can go smoothly from activity coefficient-like behavior to classical van der Waals one-fluid mixing rule by mere variation of its parameters. The parameters in this reformulated mixing rule can be obtained from correlating VLE data or from the two infinite dilution activity coefficients for each binary pair in the mixture. Together with UNIFAC, this mixing rule becomes completely predictive.

4. The NRTL model

The concept of local composition was successfully used by Renon and Prausnitz [21] to derive the NRTL equation for the excess Gibbs free energy. The NRTL equation for the binary system is given by

$$\frac{G^E}{RT} = x_1 x_2 \left[\frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_2 + x_1 G_{12}}\right] \qquad (16)$$

where,

$$\tau_{12} = \frac{g_{12} - g_{22}}{RT} \text{ and } \tau_{21} = \frac{g_{21} - g_{11}}{RT} \qquad (17)$$

$$G_{12} = \exp(-\alpha_{12}\tau_{12}) \text{ and } G_{21} = \exp(-\alpha_{12}\tau_{21}) \qquad (18)$$

The parameter α_{12} is related to the randomness of the mixture. When α_{12} is zero, the mixture is completely random. Actually the NRTL equation contains three parameters, but reduction of experimental data for a large number of binary systems indicates that α_{12} varies from about 0.20 to 0.47. When experimental data are not available, the value of α_{12} may be set arbitrarily to 0.3. The activity coefficient equations are given by

$$\ln\gamma_1 = x_2^2 \left[\tau_{21}\left(\frac{G_{21}}{x_1 + x_2 G_{21}}\right)^2 + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2}\right] \qquad (19)$$

$$\ln\gamma_2 = x_1^2 \left[\tau_{12}\left(\frac{G_{12}}{x_2 + x_1 G_{12}}\right)^2 + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2}\right] \qquad (20)$$

For highly nonideal mixtures and for partially immiscible systems, the NRTL equation often provides a good representation of experimental data. The NRTL equation can be readily generalized to multicomponent mixtures also.

5. Results and discussion

The PRSV κ_1 for each pure compound was optimized within the temperature range in which their VLE has been studied. The simplex algorithm of Nelder and Mead [25] was used with the following objective function

$$\min I_i = \sum_{i=1}^{n} \left[\frac{P_{\text{exp}}(i) - P_{\text{calc}}(i)}{P_{\text{exp}}(i)}\right]^2 \qquad (21)$$

where P_{exp} is the observed vapor pressure and P_{calc} is the calculated vapor pressure. Vapor pressure data for pure components were collected from DIPPR data compilation [26].

Table 1
Physical properties of the pure components and the PRSV κ_1 parameters

No.	Compound	T_c, K	P_c, bar	ω	T range, K	n	PRSV κ_1	ΔP, bar
1	Acetaldehyde	461.00	55.50	0.3167	275–375	11	−0.2533	0.0560
2	Acetone	508.20	47.02	0.3064	275–375	11	−0.0030	0.0001
3	Acetic Acid	592.71	57.86	0.4624	300–400	11	−0.2067	0.0001
4	Aniline	699.00	53.09	0.4041	350–450	11	−0.0950	0.0090
5	Benzene	562.16	48.98	0.2108	275–375	11	0.0642	0.0020
6	Bromobenzene	670.15	45.19	0.2506	350–450	11	0.0338	0.0040
7	1-butanol	562.93	44.13	0.5945	275–375	11	0.2415	0.0020
8	2-butanol	536.01	41.94	0.5711	275–375	11	0.3641	0.0020
9	*t*-butanol	506.20	39.72	0.6158	275–375	11	0.4029	0.0001
10	2-butanone	535.50	41.54	0.3241	275–375	11	−0.0357	0.0010
11	1-butene	419.59	40.20	0.1867	275–345	8	0.0641	0.0080
12	1,2-Butylene oxide	526.00	43.90	0.2348	275–375	11	0.0823	0.0001
13	Chloroform	536.40	54.72	0.2129	275–375	11	0.0531	0.0030
14	Croton aldehyde	571.00	42.50	0.3455	300–400	11	0.0401	0.0001
15	Cyclohexane	553.54	40.75	0.2118	275–375	11	0.0488	0.0010
16	Cyclohexanol	625.15	37.49	0.5141	350–450	11	0.4146	0.0020
17	Cyclohexanone	629.15	38.50	0.4500	300–400	11	−0.2611	0.0020
18	*n*-decane	618.45	21.23	0.4842	275–375	11	0.0423	0.0010
19	1,2-dichloroethane	561.00	53.70	0.2876	300–400	11	−0.0556	0.0020
20	Diethylene glycol	680.00	46.00	1.2006	375–475	11	−0.9509	0.0010
21	Dimethoxy methane	480.60	39.52	0.2904	275–375	11	0.0635	0.0040
22	1,4-dioxane	587.00	52.08	0.2804	300–400	11	0.0217	0.0030
23	1,2-ethanediol	645.00	75.30	1.1367	350–450	11	−1.0221	0.0020
24	Ethyl acetate	523.25	38.30	0.3611	275–375	11	0.0693	0.0001
25	Ethyl benzene	617.17	36.09	0.3036	300–400	11	0.0340	0.0001
26	Ethyl cyclohexane	609.15	30.40	0.2455	275–425	13	0.1359	0.0001
27	Furfural	657.00	55.12	0.4442	275–375	11	−0.1195	0.0001
28	*n*-heptane	540.26	27.36	0.3511	275–375	11	0.0297	0.0010
29	*n*-hexane	507.43	30.12	0.3046	275–375	11	−0.0154	0.0040
30	1-hexanol	611.35	35.10	0.5803	275–375	11	0.2589	0.0001
31	2-methoxy ethanol	564.00	50.10	0.7311	275–375	11	−0.4560	0.0060
32	Methyl acetate	506.80	46.90	0.3253	275–375	11	0.0353	0.0010
33	*N*-methyl aniline	701.55	51.98	0.4799	350–450	11	−0.2138	0.0030
34	3-Methyl butanol	579.45	38.80	0.5558	300–400	11	0.4450	0.0020
35	Methyl cyclohexane	572.19	34.71	0.2350	275–375	11	0.0601	0.0030
36	Methyl methacrylate	564.00	36.80	0.3168	275–375	11	0.0404	0.0090
37	2-methyl-1-propanol	547.73	42.95	0.5885	275–400	13	0.4062	0.0010
38	3-pentanone	560.95	37.39	0.3502	300–400	11	−0.0084	0.0001
39	1-pentanol	586.15	38.80	0.5938	275–375	11	0.2659	0.0010
40	2-propanol	508.31	47.64	0.6689	275–375	11	0.0836	0.0030
41	Propionic acid	612.00	53.702	0.5444	300–400	11	−0.0321	0.0040
42	1,2-Propylene oxide	482.25	49.24	0.2710	275–375	11	−0.0492	0.0130
43	Sulfolane	849.00	50.30	0.3824	325–425	11	0.0471	0.0001
44	1,1,2,2,-tetrachloro ethane	624.00	40.20	0.2422	275–400	13	0.1166	0.0030
45	Toluene	591.79	41.09	0.2641	300–400	11	0.0319	0.0020
46	Vinyl acetate	524.00	42.50	0.3384	275–375	11	0.0529	0.0030
47	*O*-xylene	630.37	37.34	0.3127	375–475	11	0.0013	0.0020

The P_c, T_c and ω values for each pure compound were also taken from the same source. The reduction in temperature range resulted in κ_1 values which almost always predicted better results in terms of the pure component vapor pressure. The physical properties of pure compounds (T_c, P_c and ω), the κ_1 parameter, number of data points used in optimization and the errors in vapor pressure (ΔP) are shown in Table 1.

The values of κ_1 thus obtained are then used to correlate the experimental VLE data to obtain the binary interaction parameter k_{12} and the NRTL model parameters τ_{12}, τ_{21} and α_{12}. The following function was minimized

$$\min I_2 = \sum_{i=1}^{n}\left[\frac{P_{\exp}(i) - P_{\text{calc}}(i)}{P_{\exp}(i)}\right]^2 + \sum_{i=1}^{n}\left[\frac{y_{\exp}(i) - y_{\text{calc}}(i)}{y_{\exp}(i)}\right]^2 \qquad (22)$$

using simplex algorithm. The experimental P–x–y data were collected from DECHEMA data series [27,28] and DIPPR data series [29,30]. Several checks were made to ensure that the computer code is free from errors. Initial guesses of the three parameters (k_{12}, τ_{12} and τ_{21}) were supplied from a two

Table 2
Parameters obtained from optimization

No.	System	T, K	n	k_{12} (opt)	b_1/b_2	NRTL model parameters from optimization			Errors		Errors reported in DECHEMA	
						α_{12}	τ_{12}	τ_{21}	Δy	ΔP,bar	Δy	ΔP,bar
1	Acetaldehyde/Acetone [a]	298.15	8	0.061	0.77	0.80	-0.4686	0.5748	0.0272	0.0043	–	–
		348.15	8	0.030		0.05	-0.3093	0.3052	0.0153	0.0374	–	–
2	Acetaldehyde/1,2-propylene oxide [b]	298.15	8	0.000	0.85	0.10	-0.0591	0.2978	0.0115	0.0030	–	–
		348.15	8	0.100		0.25	-0.6112	0.2525	0.0085	0.0547	–	–
3	Acetone/Chloroform	301.30	8	0.101	1.10	0.30	-1.4099	0.2367	0.0110	0.0027	0.0160	0.0034
		313.55	9	0.100		0.30	-1.3140	0.2504	0.0070	0.0039	0.0107	0.0069
		328.25	11	0.053		0.30	-1.4099	0.2417	0.0090	0.0210	0.0080	0.0064
4	Acetone/Crotonaldehyde	298.15	12	0.021	0.81	0.30	0.3048	0.7015	0.0287	0.0017	0.0018	0.0014
		313.15	12	0.099		0.30	-0.0344	0.2795	0.0244	0.0022	0.0031	0.0022
		328.15	12	-0.006		0.30	0.6902	0.3249	0.0209	0.0024	0.0062	0.0062
5	Acetone/Cyclohexane	308.15	11	0.260	0.80	0.30	0.3909	1.6113	0.0061	0.0022	0.0074	0.0025
		318.15	11	0.158		0.30	0.7399	1.5751	0.0052	0.0029	0.0056	0.0051
		328.15	11	0.093		0.30	1.0134	1.4652	0.0050	0.0031	0.0046	0.0158
6	Acetone/*n*-decane	313.15	11	0.129	0.37	0.30	4.0309	0.8950	0.0008	0.0052	0.0012	0.0154
		333.15	13	0.102		0.30	3.8243	1.1158	0.0026	0.0091	0.0005	0.0498
7	Acetone/*n*-heptane	323.15	11	0.043	0.55	0.30	2.3564	0.6689	0.0053	0.0020	0.0156	0.0076
		338.15	8	0.082		0.30	2.2532	0.5414	0.0194	0.0163	0.0145	0.0341
8	Acetone/*n*-hexane	293.15	16	0.073	0.64	0.30	1.4315	1.4799	0.0031	0.0015	0.0064	0.0015
		308.15	11	0.064		0.30	1.5993	1.3226	0.0084	0.0031	0.0141	0.0088
		318.15	11	0.049		0.30	1.6291	1.2963	0.0049	0.0018	0.0091	0.0074
		328.15	11	0.018		0.30	1.5953	1.2972	0.0073	0.0037	0.0091	0.0074
9	Acetone/Toluene	308.15	14	-0.027	0.75	0.30	0.5022	0.4414	0.0032	0.0008	0.0061	0.0035
		318.15	15	0.025		0.30	0.1696	0.6420	0.0028	0.0014	0.0033	0.0054
		328.15	15	0.026		0.30	0.3447	0.4492	0.0033	0.0012	0.0051	0.0116
10	Acetone/Vinyl acetate	298.15	13	0.100	0.88	0.30	-0.2407	0.2989	0.0043	0.0010	0.0018	0.0014
		308.15	11	0.050		0.30	-0.0971	0.3033	0.0029	0.0014	0.0017	0.0016
		323.15	15	-0.023		0.30	-0.0461	0.5450	0.0032	0.0012	0.0029	0.0038
11	Aniline/1,2-ethanediol	393.15	11	0.250	1.54	0.30	-0.0596	0.3080	0.0415	0.0082	0.0030	0.0006
		418.15	10	0.162		0.30	1.0828	0.5279	0.0141	0.0029	0.0032	0.0021
12	Benzene/1-butanol	298.15	7	0.105	0.90	0.30	1.9326	0.1298	0.0040	0.0012	0.0073	0.0061
		318.15	9	0.117		0.30	2.1347	-0.0376	0.0032	0.0023	0.0044	0.0035
13	Benzene/2-butanol	298.15	6	0.108	0.90	0.30	2.2114	0.0347	0.0098	0.0004	0.0243	0.0050
		318.15	12	0.089		0.30	1.8978	0.0759	0.0056	0.0020	0.0044	0.0020
		333.15	9	0.096		0.30	2.4056	-0.0935	0.0172	0.0042	0.0115	0.0150
		343.15	10	0.264		0.30	2.4598	-0.8770	0.0091	0.0027	0.0121	0.0030
		353.15	10	0.100		0.30	0.8674	0.3099	0.0073	0.0154	0.0076	0.0171
14	Benzene/*t*-butanol	298.15	7	0.100	0.90	0.30	1.8200	0.2744	0.0123	0.0012	0.0097	0.0032
		318.15	13	0.054		0.30	1.8914	0.2011	0.0048	0.0014	0.0093	0.0019
		333.15	8	0.100		0.30	1.4217	0.3186	0.0155	0.0039	0.0108	0.0128
		343.15	10	0.112		0.30	1.4735	0.0805	0.0090	0.0035	0.0172	0.0231
		353.15	8	0.099		0.30	-0.5572	-0.0703	0.1129	0.0366	0.0224	0.1186
15	Benzene/Methyl methacrylate [c]	323.15	10	0.012	1.34	0.30	-0.1387	0.5748	0.0026	0.0018	–	–
		343.15	10	-0.029		0.30	0.0080	0.5418	0.0033	0.0036	–	–
		363.15	10	0.029		0.30	-0.2042	0.5884	0.0036	0.0067	–	–
16	Bromo benzene/Cyclohexanol	383.15	11	0.099	0.89	0.30	0.7200	0.2640	0.0049	0.0016	0.0068	0.0014
		403.15	11	0.017		0.30	0.4368	0.2973	0.0069	0.0016	0.0038	0.0036
17	2-butanone/Acetic Acid	341.66	11	0.109	1.26	0.30	-0.1868	-0.2269	0.0227	0.0268	0.0092	0.0244
		351.15	11	0.101		0.30	-0.6699	0.2825	0.0179	0.0110	0.0092	0.0121
18	2-butanone/Ethyl benzene	328.15	14	-0.580	0.75	0.30	1.8456	0.5040	0.0046	0.0052	0.0111	0.0075
		338.15	16	-0.005		0.30	0.1711	0.3651	0.0036	0.0039	0.0039	0.0050
		348.15	15	0.049		0.30	0.1093	0.3122	0.0045	0.0047	0.0088	0.0173
19	2-butanone/2-methoxy ethanol	343.15	11	0.101	1.15	0.40	0.4350	0.1808	0.0339	0.0059	0.0115	0.0142
		353.15	10	0.049		0.40	0.4991	0.2843	0.0296	0.0104	0.0100	0.0138
		363.15	5	0.020		0.40	0.7200	0.2947	0.0401	0.0074	0.0185	0.0207
20	2-butanone/2-propanol	323.15	14	0.200	1.21	0.30	-0.1647	0.3242	0.0166	0.0028	0.0164	0.0087

(*continued*)

Table 2 (*continued*)

No.	System	T, K	n	k_{12} (opt)	b_1/b_2	NRTL model parameters from optimization			Errors		Errors reported in DECHEMA	
						α_{12}	τ_{12}	τ_{21}	Δy	ΔP,bar	Δy	ΔP,bar
		328.15	9	0.100		0.30	0.2427	0.2972	0.0054	0.0035	0.0105	0.0092
21	2-butanone/Propionic Acid	343.15	12	0.100	1.13	0.30	−0.6092	0.2880	0.0201	0.0101	0.0059	0.0153
		352.15	12	0.100		0.30	−0.6424	0.2826	0.0160	0.0184	0.0069	0.0196
22	2-butanone/Toluene	318.15	15	−0.040	0.90	0.30	−0.5086	1.2178	0.0040	0.0031	0.0035	0.0040
		328.15	14	−0.247		0.30	0.1263	0.9331	0.0049	0.0029	0.0035	0.0036
		348.15	14	−0.431		0.30	0.9226	0.7522	0.0029	0.0018	0.0049	0.0043
23	1-butene/Furfural	310.95	11	0.047	0.88	0.20	2.8727	0.1857	0.0005	0.0366	0.0008	0.0783
		324.85	7	0.000		0.20	2.6967	0.2930	0.0012	0.0351	0.0021	0.0647
24	1,2-butylene oxide/methyl acetate [d]	298.15	9	0.111	1.11	0.50	2.9158	0.0154	0.0448	0.0420	–	–
		348.15	10	0.100		0.30	−0.2815	0.3081	0.0618	0.0126	–	–
25	Croton aldehyde/Acetic acid	323.15	12	0.000	1.31	0.30	0.1443	0.2946	0.0452	0.0041	0.0077	0.0032
		348.15	12	−0.003		0.30	−0.1100	0.3100	0.0294	0.0049	0.0114	0.0041
		373.15	12	0.000		0.30	−0.0326	0.2743	0.0313	0.0119	0.0079	0.0247
26	Cyclohexane/Cyclohexanone	323.15	13	0.057	0.83	0.30	1.6446	0.0849	0.0055	0.0027	0.0059	0.0032
		348.15	14	0.097		0.30	1.3026	0.1105	0.0694	0.0428	0.0105	0.0153
27	Cyclohexane/1-hexanol	323.15	13	0.194	0.78	0.30	2.5242	−0.3908	0.0030	0.0059	0.0021	0.0125
		333.15	14	0.327		0.30	1.7168	−0.4825	0.0037	0.0103	0.0107	0.0338
		343.15	15	0.443		0.30	1.6673	−0.7955	0.0095	0.0108	0.0076	0.0095
		354.35	18	0.243		0.30	1.9804	−0.4183	0.0046	0.0138	0.0029	0.0255
28	Cyclohexane/2-propanol	313.15	6	0.100	1.27	0.30	3.0279	0.3338	0.0091	0.0016	0.0114	0.0083
		323.15	9	0.093		0.30	2.6696	0.5887	0.0117	0.0042	0.0102	0.0065
		328.15	6	0.152		0.30	2.4723	0.3219	0.0023	0.0018	0.0103	0.0107
		333.15	10	0.150		0.30	2.5841	0.3640	0.0096	0.0026	0.0079	0.0064
		342.15	6	0.150		0.30	2.5717	0.3189	0.0033	0.0029	0.0085	0.0176
29	1,2-dichloro ethane/3-methyl butanol	323.15	11	0.100	0.70	0.30	1.2812	0.3000	0.0038	0.0009	0.0075	0.0065
		333.15	11	0.138		0.30	1.2383	0.1482	0.0064	0.0035	0.0103	0.0112
		343.15	11	0.117		0.30	1.1586	0.2336	0.0059	0.0029	0.0075	0.0096
		353.15	11	0.100		0.30	1.0672	0.3055	0.0060	0.0023	0.0057	0.0046
30	1,2-dichloro ethane/2-methyl-1-propanol	323.15	11	0.128	0.82	0.30	2.0721	−0.0765	0.0057	0.0016	0.0049	0.0031
		333.15	11	0.038		0.30	2.2557	−0.1295	0.0068	0.0034	0.0063	0.0067
		343.15	11	0.107		0.30	1.8879	−0.0416	0.0088	0.0031	0.0060	0.0046
		353.15	11	0.012		0.30	1.6200	0.3313	0.0144	0.0037	0.0058	0.0113
31	Dimethoxy methane/Chloroform	298.15	11	0.051	1.24	0.30	−1.1885	0.8382	0.0130	0.0105	0.0078	0.0152
		308.15	11	0.101		0.30	−0.9502	−0.4196	0.0015	0.0012	0.0005	0.0004
32	1,4-dioxane/2-methyl-1-propanol	353.15	9	0.100	0.8800	0.30	0.0287	0.2900	0.0082	0.0023	0.0081	0.0090
		373.15	9	0.101		0.30	−0.1409	0.3011	0.0063	0.0025	0.0064	0.0129
33	Ethyl acetate/2-propanol	313.15	14	0.200	1.28	0.30	0.2565	0.2841	0.0110	0.0024	0.0084	0.0031
		328.15	12	0.145		0.30	1.1896	−0.3452	0.0043	0.0016	0.0144	0.0040
		333.15	19	0.233		0.30	0.6364	−0.2965	0.0052	0.0035	0.0125	0.0048
34	Ethyl acetate/2-methoxy ethanol	343.15	15	0.185	1.21	0.30	0.5359	−0.0521	0.0214	0.0080	0.0113	0.0054
		353.14	14	0.100		0.30	0.3108	0.3000	0.0179	0.0118	0.0040	0.0063
		363.15	10	0.100		0.30	0.3347	0.3000	0.0181	0.0085	0.0057	0.0106
35	Ethyl cyclohexane/Sulfolane [c]	377.75	6	0.021	1.19	0.30	3.8314	3.0200	0.0004	0.0018	–	–
		405.15	6	0.017		0.30	4.1125	2.7200	0.0008	0.0011	–	–
36	Heptane/3-pentanone	338.15	17	0.079	1.32	0.30	0.9755	0.2787	0.0076	0.0009	0.0104	0.0019
		353.15	17	0.050		0.30	1.0217	0.3000	0.0058	0.0024	0.0056	0.0032
		368.15	17	0.050		0.30	0.9200	0.3162	0.0059	0.0043	0.0028	0.0071
37	Hexane/1-pentanol	298.15	11	0.091	1.12	0.30	2.6975	−0.0490	0.0006	0.0025	0.0006	0.0046
		303.15	15	0.121		0.30	2.3112	0.0623	0.0054	0.0028	0.0043	0.0044
		323.15	15	0.135		0.30	2.2909	0.0089	0.0061	0.0060	0.0047	0.0055
38	*N*-methyl aniline/1,2-ethanediol	368.15	13	0.074	1.58	0.30	1.3253	1.9011	0.0187	0.0005	0.0131	0.0005

(*continued*)

Table 2 (*continued*)

No.	System	T, K	n	k_{12} (opt)	b_1/b_2	NRTL model parameters from optimization			Errors		Errors reported in DECHEMA	
						α_{12}	τ_{12}	τ_{21}	Δy	ΔP,bar	Δy	ΔP,bar
		393.15	15	0.101		0.30	1.5946	1.6687	0.0157	0.0011	0.0054	0.0009
		418.15	14	0.115		0.30	1.5577	1.6099	0.0185	0.0025	0.0051	0.0021
39	2-methyl-1-propanol/ 1,1,2,2-tetrachloro ethane	353.15	15	0.438	0.82	1.00	−1.0281	0.1510	0.0989	0.0117	0.0122	0.0040
		368.15	14	0.457		1.00	−1.1996	0.5030	0.0603	0.0207	0.0168	0.0190
		380.15	13	0.334		1.00	−0.8904	0.3788	0.0993	0.0316	0.0063	0.0165
40	2-propanol/*n*-heptane	318.15	18	−0.0549	0.54	0.30	1.6430	2.5316	0.0211	0.0040	0.0078	0.0047
		333.15	18	−0.0048		0.30	1.5103	2.4221	0.0148	0.0064	0.0063	0.0081
41	2-propanol/methyl cyclohexane	323.15	10	−0.3900	0.65	0.25	2.2448	2.7144	0.0112	0.0029	0.0067	0.0038
		333.15	12	0.2315		0.30	0.2818	2.4458	0.0117	0.0066	0.0084	0.0091
42	Toluene/1-butanol	363.15	16	0.102	1.13	0.30	1.4200	0.3220	0.0157	0.0036	0.0097	0.0160
		373.15	10	0.100		0.30	1.1509	0.3005	0.0067	0.0032	0.0089	0.0081
43	*O*-xylene/diethylene glycol	398.15	5	0.098	1.14	0.30	3.7415	1.1219	0.0044	0.0107	0.0064	0.0161
		423.15	6	0.108		0.30	2.6817	0.9994	0.0037	0.0141	0.0186	0.0246

[a] Experimental VLE data collected from Ref. [29].
[b] Experimental VLE data collected from Ref. [29].
[c] VLE data generated using UNIFAC model.
[d] Experimental VLE data collected from Ref. [29]
[e] Experimental VLE data collected from Ref. [30]

fit program that optimizes the latter two parameters for a given value of k_{12}. Several values of α_{12} were tried to reach the minimum of the objective function. Also, the program was restarted at the point where it claims to have found a minimum. The parameters thus obtained from optimization are reported in Tables 2 and 3 for each of the systems at different temperatures. The last two columns in Tables 2 and 3 show the errors reported in DECHEMA data series [27,28] using the γ–ϕ approach (NRTL model in the liquid phase and the ideal gas law in the gas phase). It can be seen that the PRSV–WSMR predictions, in general, match closely with the DECHEMA predictions. In some cases even better results are obtained using the PRSV–WSMR combination. Even for comparatively large asymmetric systems, like, acetone/*n*-decane or *N*-methyl aniline/1,2-ethanediol, we observe that the results obtained are quite good. A constant value of $\alpha_{12}(=0.3)$ was found to be applicable for many systems and in general (apart from a few exceptions) is invariant with temperature. That leaves k_{12}, τ_{12} and τ_{21} as functions of temperature. Unfortunately, the NRTL model parameters τ_{12} and τ_{21} are more sensitive towards temperature than the UNIQUAC parameters. However, in our work, the NRTL model was found to give better results than UNIQUAC in most of the situations and hence we used it exclusively.

From the results shown in Tables 2 and 3, it can be seen that the binary interaction parameter, k_{12}, is composition independent to a large extent. This composition independence keeps the mixing rule theoretically correct. However, in some situations, as reported in Tables 2 and 3, comparison with DECHEMA results indicate that the PRSV–WSMR prediction is slightly poor. Since the working pressure range in all these situations is quite low, this discrepancy may be attributed to the asymmetric nature of these systems. Some of the results from Tables 2 and 3 are shown graphically in Figs. 1–5.

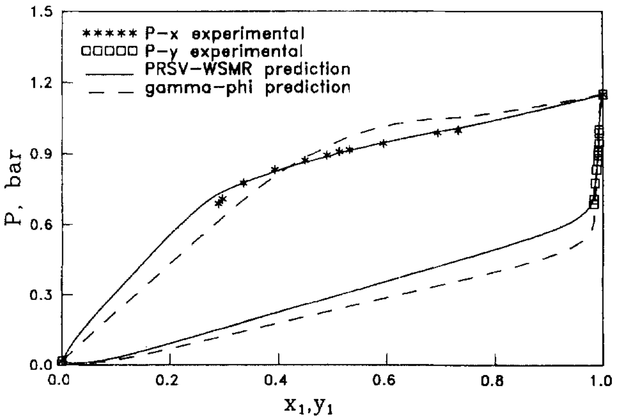

Fig. 1. P–x–y diagram for Acetone (1)/*n*-decane (2) system at 60°C.

6. Conclusion

The Peng–Robinson equation of state modified by Stryjek and Vera, known as one of the most applicable to multicomponent systems is used for computer-aided determination of optimum parameters with Wong–Sandler mixing rules. The NRTL model has been found to be suitable as a G^E model. The input data for computation are critical temperatures, critical pressures, acentric factors, the PRSV κ_1 parameters (obtained by optimization of experimental vapor pressure data) [for pure compounds], temperature at which VLE is to be computed and experimental VLE data. Results obtained

Table 3
Parameters obtained from optimization

No.	System	T, K	n	k_{12} (opt)	b_1/b_2	NRTL model parameters from optimization			Errors		Errors reported in DECHEMA	
						α_{12}	τ_{12}	τ_{21}	Δy	ΔP,bar	Δy	ΔP,bar
23	1-butene/Furfural	310.95	11	0.047	0.88	0.20	2.8727	0.1857	0.0005	0.0366	0.0008	0.0783
		324.85	7	0.000		0.20	2.6967	0.2930	0.0012	0.0351	0.0021	0.0647
24	1,2-butylene oxide/methyl acetate [a]	298.15	9	0.111	1.11	0.50	2.9158	0.0154	0.0448	0.0420	–	–
		348.15	10	0.100		0.30	−0.2815	0.3081	0.0618	0.0126	–	–
25	Croton aldehyde/Acetic acid	323.15	12	0.000	1.31	0.30	0.1443	0.2946	0.0452	0.0041	0.0077	0.0032
		348.15	12	−0.003		0.30	−0.1100	0.3100	0.0294	0.0049	0.0114	0.0041
		373.15	12	0.000		0.30	−0.0326	0.2743	0.0313	0.0119	0.0079	0.0247
26	Cyclohexane/Cyclohexanone	323.15	13	0.057	0.83	0.30	1.6446	0.0849	0.0055	0.0027	0.0059	0.0032
		348.15	14	0.097		0.30	1.3026	0.1105	0.0694	0.0428	0.0105	0.0153
27	Cyclohexane/1-hexanol	323.15	13	0.194	0.78	0.30	2.5242	−0.3908	0.0030	0.0059	0.0021	0.0125
		333.15	14	0.327		0.30	1.7168	−0.4825	0.0037	0.0103	0.0107	0.0338
		343.15	15	0.443		0.30	1.6673	−0.7955	0.0095	0.0108	0.0076	0.0095
		354.35	18	0.243		0.30	1.9804	−0.4183	0.0046	0.0138	0.0029	0.0255
28	Cyclohexane/2-propanol	313.15	6	0.100	1.27	0.30	3.0279	0.3338	0.0091	0.0016	0.0114	0.0083
		323.15	9	0.093		0.30	2.6696	0.5887	0.0117	0.0042	0.0102	0.0065
		328.15	6	0.152		0.30	2.4723	0.3219	0.0023	0.0018	0.0103	0.0107
		333.15	10	0.150		0.30	2.5841	0.3640	0.0096	0.0026	0.0079	0.0064
		342.15	6	0.150		0.30	2.5717	0.3189	0.0033	0.0029	0.0085	0.0176
29	1,2-dichloro ethane/3-methyl butanol	323.15	11	0.100	0.70	0.30	1.2812	0.3000	0.0038	0.0009	0.0075	0.0065
		333.15	11	0.138		0.30	1.2383	0.1482	0.0064	0.0035	0.0103	0.0112
		343.15	11	0.117		0.30	1.1586	0.2336	0.0059	0.0029	0.0075	0.0096
		353.15	11	0.100		0.30	1.0672	0.3055	0.0060	0.0023	0.0057	0.0046
30	1,2-dichloro ethane/2-methyl-1-propanol	323.15	11	0.128	0.82	0.30	2.0721	−0.0765	0.0057	0.0016	0.0049	0.0031
		333.15	11	0.038		0.30	2.2557	−0.1295	0.0068	0.0034	0.0063	0.0067
		343.15	11	0.107		0.30	1.8879	−0.0416	0.0088	0.0031	0.0060	0.0046
		353.15	11	0.012		0.30	1.6200	0.3313	0.0144	0.0037	0.0058	0.0113
31	Dimethoxy methane/Chloroform	298.15	11	0.051	1.24	0.30	−1.1885	0.8382	0.0130	0.0105	0.0078	0.0152
		308.15	11	0.101		0.30	−0.9502	−0.4196	0.0015	0.0012	0.0005	0.0004
32	1,4-dioxane/2-methyl-1-propanol	353.15	9	0.100	0.8800	0.30	0.0287	0.2900	0.0082	0.0023	0.0081	0.0090
		373.15	9	0.101		0.30	−0.1409	0.3011	0.0063	0.0025	0.0064	0.0129
33	Ethyl acetate/2-propanol	313.15	14	0.200	1.28	0.30	0.2565	0.2841	0.0110	0.0024	0.0084	0.0031
		328.15	12	0.145		0.30	1.1896	−0.3452	0.0043	0.0016	0.0144	0.0040
		333.15	19	0.233		0.30	0.6364	−0.2965	0.0052	0.0035	0.0125	0.0048
34	Ethyl acetate/2-methoxy ethanol	343.15	15	0.185	1.21	0.30	0.5359	−0.0521	0.0214	0.0080	0.0113	0.0054
		353.14	14	0.100		0.30	0.3108	0.3000	0.0179	0.0118	0.0040	0.0063
		363.15	10	0.100		0.30	0.3347	0.3000	0.0181	0.0085	0.0057	0.0106
35	Ethyl cyclohexane/Sulfolane [b]	377.75	6	0.021	1.19	0.30	3.8314	3.0200	0.0004	0.0018	–	–
		405.15	6	0.017		0.30	4.1125	2.7200	0.0008	0.0011	–	–
36	Heptane/3-pentanone	338.15	17	0.079	1.32	0.30	0.9755	0.2787	0.0076	0.0009	0.0104	0.0019
		353.15	17	0.050		0.30	1.0217	0.3000	0.0058	0.0024	0.0056	0.0032
		368.15	17	0.050		0.30	0.9200	0.3162	0.0059	0.0043	0.0028	0.0071
37	Hexane/1-pentanol	298.15	11	0.091	1.12	0.30	2.6975	−0.0490	0.0006	0.0025	0.0006	0.0046
		303.15	15	0.121		0.30	2.3112	0.0623	0.0054	0.0028	0.0043	0.0044
		323.15	15	0.135		0.30	2.2909	0.0089	0.0061	0.0060	0.0047	0.0055
38	*N*-methyl aniline/1,2-ethanediol	368.15	13	0.074	1.58	0.30	1.3253	1.9011	0.0187	0.0005	0.0131	0.0005
		393.15	15	0.101		0.30	1.5946	1.6687	0.0157	0.0011	0.0054	0.0009
		418.15	14	0.115		0.30	1.5577	1.6099	0.0185	0.0025	0.0051	0.0021
39	2-methyl-1-propanol/1,1,2,2-tetrachloro ethane	353.15	15	0.438	0.82	1.00	−1.0281	0.1510	0.0989	0.0117	0.0122	0.0040
		368.15	14	0.457		1.00	−1.1996	0.5030	0.0603	0.0207	0.0168	0.0190
		380.15	13	0.334		1.00	−0.8904	0.3788	0.0993	0.0316	0.0063	0.0165
40	2-propanol/*n*-heptane	318.15	18	−0.0549	0.54	0.30	1.6430	2.5316	0.0211	0.0040	0.0078	0.0047
		333.15	18	−0.0048		0.30	1.5103	2.4221	0.0148	0.0064	0.0063	0.0081

(*continued*)

Table 3 (*continued*)

No.	System	T, K	n	k_{12} (opt)	b_1/b_2	NRTL model parameters from optimization			Errors		Errors reported in DECHEMA	
						α_{12}	τ_{12}	τ_{21}	Δy	ΔP,bar	Δy	ΔP,bar
41	2-propanol/methyl cyclohexane	323.15	10	−0.3900	0.65	0.25	2.2448	2.7144	0.0112	0.0029	0.0067	0.0038
		333.15	12	0.2315		0.30	0.2818	2.4458	0.0117	0.0066	0.0084	0.0091
42	Toluene/1-butanol	363.15	16	0.102	1.13	0.30	1.4200	0.3220	0.0157	0.0036	0.0097	0.0160
		373.15	10	0.100		0.30	1.1509	0.3005	0.0067	0.0032	0.0089	0.0081
43	*O*-xylene/diethylene glycol	398.15	5	0.098	1.14	0.30	3.7415	1.1219	0.0044	0.0107	0.0064	0.0161
		423.15	6	0.108		0.30	2.6817	0.9994	0.0037	0.0141	0.0186	0.0246

[a] Experimental VLE data collected from Ref. [29].

[b] Experimental VLE data collected from Ref. [30].

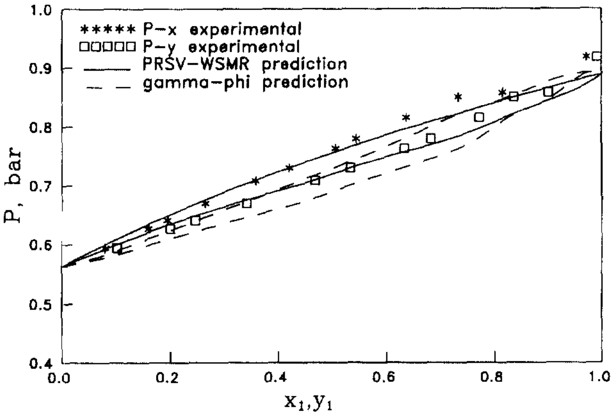

Fig. 2. *P–x–y* diagram for Crotonaldehyde (1)/Acetic acid (2) system at 100°C.

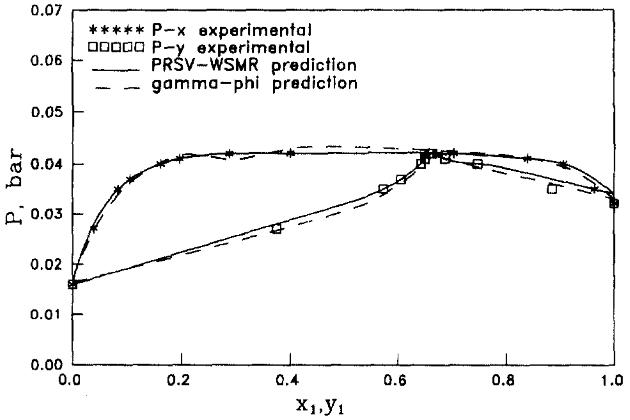

Fig. 4. *P–x–y* diagram for *N*-methyl aniline (1)/1,2-ethanediol (2) system at 95°C.

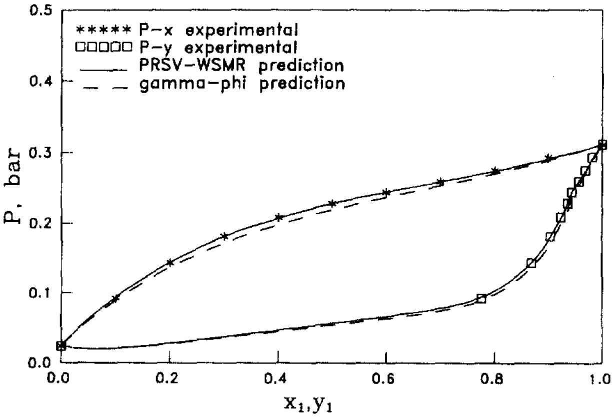

Fig. 3. *P–x–y* diagram for 1,2-dichloroethane (1)/3-methyl butanol (2) system at 50°C.

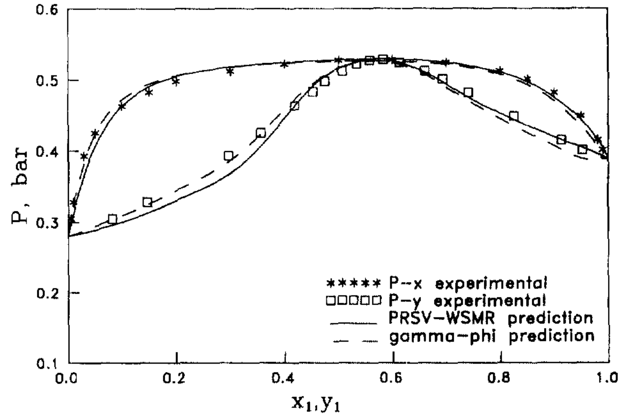

Fig. 5. *P–x–y* diagram for 2-propanol (1)/*n*-heptane (2) system at 60°C.

are quite comparable with those reported in DECHEMA data series in almost all the cases (and sometimes better) as well as for the systems that have a good degree of asymmetry. The VLE of binary or multicomponent systems can be computed from the parameters listed in Tables 1–3. Furthermore, with these parameters, the number of theoretical plates (NTP) in a distillation column can be calculated. The effect of system asymmetry on binary interaction parameter k_{ij} is noticeable in some cases. However, composition dependence of k_{ij} was not attempted in this work.

7. Nomenclature

A^E	excess Helmholtz free energy
A^E_{EoS}	excess Helmholtz free energy from equation of state
A^E_∞	excess Helmholtz free energy at infinite pressure
a	attraction parameter in equation of state
B	second virial coefficient
b	covolume parameter in equation of state

C	equation of state dependent constant in Wong–Sandler mixing rule
G	NRTL model parameter
G^E	excess Gibbs free energy
g	NRTL model parameter
I_1, I_2	objective functions to be minimized by optimization
k_{ij}	binary interaction parameter
n	number of experimental data points
P	pressure
P_c	critical pressure
R	gas constant
T	temperature
T_c	critical temperature
T_R	reduced temperature ($\equiv T/T_c$)
v	molar volume
x	liquid phase mole fraction
y	vapor phase mole fraction

Greek symbols

α	temperature correction of the equation of state attraction-term parameter 'a'
α_{12}	randomness parameter in NRTL model
γ	activity coefficient
ΔP	arithmetic average deviation in pressure ($\equiv 1/n\sum\lvert P_{\rm exp}-P_{\rm calc}\rvert$)
Δy	arithmetic average deviation in vapor phase mole fraction ($\equiv 1/n\sum\lvert y_{\rm exp}-y_{\rm calc}\rvert$)
κ, κ_0	parameters in PRSV equation of state
κ_1	characteristic parameter in PRSV equation of state depending upon the physical properties of the pure component
τ	NRTL model parameter
ϕ	fugacity coefficient
ω	acentric factor

Subscript/superscript

c	critical property
calc	calculated property
E	excess property
EoS	property calculated from PRSV equation of state with Wong–Sandler mixing rule
exp	experimental
i, j	component in a mixture
m	mixture

Acronyms

NRTL	non random two liquid model (Renon and Prausnitz, 1968)
PRSV	Peng–Robinson equation of state modified by Stryjek and Vera (1986)
UNIFAC	UNIQUAC functional group activity coefficients model (Fredenslund et al., 1975)
UNIQUAC	universal quasi–chemical model (Abrams and Prausnitz, 1975)
VLE	vapor–liquid equilibria
WSMR	Wong–Sandler mixing rules (1992)
ZRP	zero reference pressure EoS/G^E model

References

[1] A.Z. Panagiotopoulos, R.C. Reid, ACS Symp. Ser. 300 (1986) 571.
[2] Y. Adachi, H. Sugie, Fluid Phase Equilibria 23 (1986) 103.
[3] R. Sandoval, G. Wilczek-Vera, J.H. Vera, Fluid Phase Equilibria 52 (1989) 119.
[4] S. Michel, H.H. Hooper, J.M. Prausnitz, Fluid Phase Equilibria 45 (1989) 173.
[5] T.W. Copeman, P.M. Mathias, ACS Symp. Ser. 300 (1986) 352.
[6] S.I. Sandler, K.H. Lee, H. Kim, ACS Symp. Ser. 300 (1986) 180.
[7] J. Vidal, Chem. Eng. Sci. 33 (1978) 787.
[8] M.J. Huron, J. Vidal, Fluid Phase Equilibria 3 (1979) 255.
[9] J. Mollerup, Fluid Phase Equilibria 25 (1986) 323.
[10] P.A. Gupta, P. Rasmussen, A. Fredenslund, Ind. Eng. Chem. Fund. 25 (1986) 636.
[11] M.L. Michelsen, Fluid Phase Equilibria 60 (1990) 47.
[12] M.L. Michelsen, Fluid Phase Equilibria 60 (1990) 213.
[13] R.A. Heidemann, S.L. Kokal, Fluid Phase Equilibria 56 (1990) 17.
[14] D.S.H. Wong, S.I. Sandler, AIChE J. 38 (5) (1992) 671.
[15] D.S.H. Wong, H. Orbey, S.I. Sandler, Ind. Eng. Chem. Res. 31 (1992) 2033.
[16] S.I. Sandler, NATO/ASI Conference, Antalya, Turkey, July 18–30, 1993.
[17] H. Orbey, S.I. Sandler, D.S.H. Wong, Fluid Phase Equilibria 85 (1993) 41.
[18] H. Orbey, S.I. Sandler, AIChE J. 41 (3) (1995) 683.
[19] R. Stryjek, J.H. Vera, Can. J. Chem. Eng. 64 (1986) 334.
[20] R. Stryjek, J.H. Vera, Can. J. Chem. Eng. 64 (1986) 820.
[21] H. Renon, J.M. Prausnitz, AIChE J. 14 (1968) 135.
[22] D.Y. Peng, D.B. Robinson, Ind. Eng. Chem. Fund. 15 (1976) 59.
[23] P. Coutsikos, N.S. Kalospiros, D.P. Tassios, Fluid Phase Equilibria 108 (1995) 59.
[24] M.A. Satyro, M.A. Trebble, Fluid Phase Equilibria 115 (1996) 135.
[25] J.A. Nelder, R. Mead, Comput. J. 7 (1965) 308.
[26] T.E. Daubert, R.P. Danner (Eds.), Physical and thermodynamic properties of pure compounds: data compilation, Vols. 1–4, Hemisphere, New York, 1989.
[27] J. Gmehling, U. Onken, W. Arlt, Vapor–liquid equilibrium data collection. Organic hydroxy compounds: Alcohols and Phenols, DECHEMA chemistry data series, Vol. I, Part 2b, DECHEMA, Frankfurt/Main, 1978.
[28] J. Gmehling, U. Onken, W. Arlt, Vapor–liquid equilibrium data collection. Aldehydes, Ketones and Ethers, DECHEMA chemistry data series, Vol. I, Part (3+4), DECHEMA, Frankfurt/Main, 1979.
[29] A.D. Leu, D.B. Robinson, Experimental results for phase equilibria and pure properties: DIPPR data series, 1 (1991) 1.
[30] D. Zudkevitch, D. Shukla, Experimental results for phase equilibria and pure properties: DIPPR data series, 1 (1991) 32.