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The use of the *F*-function of the two-parameter cubic equation of state in vapour–liquid equilibrium calculations of binary mixtures

Guangheng Liu [1], C.J. Lim and J. Lielmezs *

Department of Chemical Engineering, The University of British Columbia, Vancouver, BC V67 1Z4 (Canada)

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Abstract

The recently developed *F*-function of Shaw and Lielmezs, Mak and Lielmezs, and Liu, Lim and Lielmezs, modified to fit the van der Waals type cubic equations of state, has been used to assess the vapour–liquid equilibria calculations of binary mixtures over a wide range of $P-T-x-y$ values.

Sets of coefficients for use in the binary interaction parameter function $L_{ij} = L_{ij}(T, P, x_i)$ were determined for 23 representative binary mixtures. The prediction (this work) of the vapour–liquid equilibria (bubble point calculations) of the binary systems considered are in excellent agreement with the experimental data, and show slight improvement over the values obtained by means of the original Redlich–Kwong–Soave (RKS) and Peng–Robinson (PR) equations.

LIST OF SYMBOLS

a, b	parameters of cubic equation of state
A, B	dimensionless parameters (eqn. (A5))
c	coefficient of *F*-function
e, f, g, h	dimensionless coefficients of eqn. (7)
F	*F*-function
FRKS	*F*-function modification of RKS equation of state
F-RKS	FRKS equation with L_{ij}-function (eqn. (7))
FPR	*F*-function modification of PR equation of state
F-PR	FPR equation with L_{ij}-function (eqn. (7))
k_{ij}	binary interaction parameter for RKS and PR equations
L_{ij}	binary interaction parameter for FRKS and FPR equations
K	vaporization equilibrium ratio

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* Corresponding author.

[1] Visiting Scholar of the Department of Chemistry, Yunnan University, Kunming, People's Republic of China.

N	number of data points
P	pressure
R	universal gas constant
T	temperature
x	composition of liquid phase
y	composition of vapour phase
Z	compressibility factor
Ω_a, Ω_b	constants of eqn. (A1)
ϕ	fugacity coefficient (eqn. (A12))

Subscripts

c	critical state
i, j, k	components of mixture
m	mixture
r	reduced state

INTRODUCTION

Recently, Liu et al. [1] extended the work of Lielmezs and co-workers [2, 3] by testing the predictive accuracy of the F-function-modified Redlich–Kwong–Soave [4] (FRKS, F-RKS) and Peng–Robinson [5] (FPR, F-PR) equations of state in calculations of P–V–T properties of binary mixtures. In this work we test the FRKS, F-RKS, FPR and F-PR equations further by including the vapour–liquid equilibria (bubble point and K value) calculations of binary systems.

The testing was done in two ways: firstly, by means of fixed isothermal and fixed averaged optimum binary interaction parameters L_{ij} independent of thermodynamic state (FRKS and FPR equations, Tables 1–4, 6), and secondly, following Lielmezs [6, 7] work by introducing instead of the fixed optimum interaction parameter L_{ij}, a binary interaction parameter L_{ij}-function of state, $L_{ij}(T, P, x_i)$ (Tables 5, 6, F-RKS, F-PR). To do this testing, experimental data from twenty-nine binary mixtures were selected from a number of sources (Tables 1–4). These literature data were considered of sufficient reliability; therefore, no further evaluation of their accuracy was made. The total set of experimental data was divided into three main groups of binary mixtures: paraffinic–paraffinic, CO_2–paraffinic and H_2S–paraffinic, and CO_2–polar and polar–polar compounds. The constants necessary to perform vapour–liquid equilibrium calculations, the T_c, P_c and acentric factor ω values and the required coefficients of the F-function for pure compounds, were taken from the work of Liu et al. [1]. The bubble-point pressures (Tables 1–3, 6) and vaporization equilibrium ratio K values (Figs. 1–3) were obtained following the general comments of calculation methods as given by Reid et al. [8], subject to the derived relations of this work (FRKS, F-RKS, FPR, F-PR) listed in the Appendix.

RESULTS AND DISCUSSION

The F-functions for the FRKS, F-RKS, FPR and F-PR equations were determined by methods already outlined by Lielmezs and co-workers [1–3, 6, 7]. Tables 1–3 compare the results of bubble-point pressure and vapour mole-fraction calculations made by means of fixed isothermal optimum binary interaction parameter k_{ij} and L_{ij} values; Table 4 lists the fixed averaged optimum binary interaction parameter k_{ij} and L_{ij} values optimized with respect to the total number of data points; Table 5 presents the coefficients of the binary interaction parameter L_{ij}-function (eqn. (7)) while Table 6 summarizes the results of bubble point calculations using different methods. Figures 1–3 compare calculated (F-RKS equation) and experimental vaporization equilibrium ratio K values taken at several isotherms for a set of binary mixtures.

The accuracy of the bubble-point pressure and vapour mole-fraction calculations was determined by means of the relative deviation of pressure ΔP (%) and the absolute deviation of vapour mole-fraction Δy, defined as

$$\Delta P\,(\%) = \frac{1}{N}\sum_i \left|\frac{P_{\mathrm{cal}} - P_{\mathrm{exp}}}{P_{\mathrm{exp}}}\right|_i \times 100 \tag{1}$$

$$\Delta y = \frac{1}{N}\sum_i |y_{\mathrm{cal}} - y_{\mathrm{exp}}|_i \times 100 \tag{2}$$

where N is the number of data points, and subscripts cal and exp represent calculated and experimental values, respectively.

Following the work of Liu et al. [1], the mixing rules for the FRKS and FPR equations are given as

$$F_{\mathrm{m}} = \frac{1}{b_{\mathrm{m}}}\sum_i \sum_j x_i x_j (b_i b_j F_i F_j)^{1/2} L_{ij} \tag{3}$$

$$b_{\mathrm{m}} = \sum_i b_i x_i \tag{4}$$

For the original RKS and PR equations of state, the conventional mixing rules have been used

$$a_{\mathrm{m}} = \sum_i \sum_j x_i x_j (a_i a_j)^{1/2}(1 - k_{ij}) \tag{5}$$

where b_{m} is the same as in eqn. (4).

TABLE 1

Comparison of the deviations (eqns. (1, 2)) in bubble point calculations using the RKS, FRKS, PR and FPR methods for paraffin–paraffin binary systems

System	Ref.	T (K)	N	RKS			FRKS			PR			FPR		
				k_{12}	ΔP (%)	Δy_1	L_{12}	ΔP (%)	Δy_1	k_{12}	ΔP (%)	Δy_1	L_{12}	ΔP (%)	Δy_1
CH_4–C_2H_6	9	144.3	7	0.00352	0.59	0.16	1.00133	2.26	0.09	0.00701	0.54	0.04	1.00132	2.22	0.09
		189.7	13	−0.00523	0.96	0.48	1.00567	1.04	0.33	0.00027	0.90	0.31	1.0	0.87	0.29
		195.4	8	0.0	1.00	0.23	0.99285	1.18	0.21	0.0	0.81	0.22	1.0	1.47	0.25
CH_4–C_3H_8	10	277.6	29	0.01815	0.81	0.90	0.93005	0.98	0.67	0.02303	1.11	0.99	0.91538	1.46	0.81
		310.9	25	0.02882	0.66	1.29	0.89199	1.26	0.98	0.02897	0.51	1.68	0.87276	1.72	1.29
		327.6	20	0.04819	0.54	0.98	0.85012	0.89	1.14	0.04532	0.59	1.33	0.84448	1.26	1.15
CH_4–nC_4H_{10}	11	294.3	20	0.02007	0.74	0.40	0.91972	1.37	0.36	0.02446	0.83	0.36	0.90254	1.68	0.44
		327.6	16	0.02944	0.67	0.74	0.87265	1.58	0.45	0.03069	0.45	0.57	0.85442	2.13	0.36
		377.6	11	0.09374	2.30	2.12	0.76570	2.51	2.49	0.08498	2.64	1.27	0.74438	3.30	1.39
CH_4–nC_5H_{12}	12	310.9	15	0.01777	0.48	0.87	0.90872	0.74	0.88	0.02318	0.48	0.64	0.88999	0.75	0.68
		344.3	14	0.02418	0.47	1.03	0.86713	0.71	0.91	0.02714	0.54	0.67	0.84704	0.93	0.54
		377.6	19	0.03769	0.49	1.24	0.81727	0.67	1.43	0.03542	0.41	0.80	0.79989	0.97	0.77
CH_4–nC_6H_{14}	13	298.2	10	0.02998	0.65	0.62	0.90853	0.73	0.59	0.03518	0.53	0.53	0.89378	0.55	0.56
		323.2	10	0.03193	0.35	0.81	0.88431	0.32	0.82	0.03503	0.41	0.81	0.86709	0.37	0.85
		373.2	10	0.04896	0.49	1.25	0.81570	0.57	1.27	0.04600	0.58	1.37	0.79867	0.63	1.36
CH_4–nC_8H_{18}	14	298.2	7	0.04016	0.87	0.05	0.90221	0.89	0.05	0.04514	0.93	0.07	0.88916	1.12	0.06
		323.2	7	0.04056	1.48	0.08	0.87839	1.52	0.08	0.04256	1.54	0.11	0.86340	1.63	0.10
		373.2	7	0.05723	2.50	0.34	0.80932	2.82	0.35	0.05478	2.53	0.49	0.79489	2.96	0.46
C_2H_6–C_3H_8	15	310.9	17	−0.00677	1.08	0.27	1.00562	0.78	0.24	−0.00562	0.93	0.28	1.00562	0.88	0.26
		322.0	12	−0.00132	1.00	0.75	1.00361	0.66	0.63	−0.00523	0.84	0.64	1.00557	0.87	0.55
		344.3	9	−0.00213	1.04	1.11	1.01398	1.49	0.91	−0.00505	1.31	0.95	0.99858	1.25	0.87
C_2H_6–nC_4H_{10}	16	338.7	6	0.03054	2.19	0.94	0.98238	1.87	0.57	0.02457	2.16	1.04	0.97907	2.14	0.99
		366.5	8	0.03790	1.67	0.98	0.97209	1.43	0.64	0.03432	1.56	1.35	0.96946	1.49	1.29
		394.3	5	0.05274	1.78	1.75	0.95731	1.63	1.01	0.04686	1.80	1.81	0.95406	1.51	1.92
C_2H_6–nC_5H_{12}	17	310.9	12	0.00245	1.33	0.44	0.99796	1.35	0.44	0.00588	1.31	0.38	0.99436	1.31	0.38
		344.3	13	0.00525	2.10	0.37	1.00352	1.45	0.39	0.00819	1.94	0.31	0.99629	1.93	0.32
		377.6	14	0.00883	1.23	1.29	1.00520	0.76	1.19	0.00849	1.09	1.34	0.99542	0.93	1.30
C_2H_6–nC_6H_{14}	18	298.2	7	0.00121	2.11	0.47	0.99783	1.97	0.43	0.00443	1.84	0.39	0.99553	1.82	0.41
C_2H_6–nC_8H_{18}	19	323.2	12	0.01251	1.31	0.96	0.98812	1.13	0.95	0.01437	1.37	0.90	0.98649	1.27	0.92
		348.2	12	0.02040	1.84	0.61	0.98764	1.86	0.57	0.02064	1.83	0.57	0.98161	1.85	0.58
		373.2	9	0.02122	1.68	1.27	0.99104	1.84	1.25	0.02078	1.72	1.18	0.98271	1.77	1.18
Average					1.18	0.80		1.30	0.72		1.16	0.76		1.45	0.72

TABLE 2

Comparison of the deviations (eqns. (1, 2)) in bubble point calculations using the RKS, FRKS, PR and FPR methods for CO_2–paraffin and H_2S–paraffin binary systems

System	Ref.	T (K)	N	RKS			FRKS			PR			FPR		
				k_{12}	ΔP (%)	Δy_1	L_{12}	ΔP (%)	Δy_1	k_{12}	ΔP (%)	Δy_1	L_{12}	ΔP (%)	Δy_1
CH_4–CO_2	20	241.5	10	0.10292	2.74	0.95	0.87480	3.51	1.09	0.09775	2.63	1.09	0.86684	3.33	1.71
		259.8	9	0.11041	2.10	1.03	0.85877	1.83	1.03	0.10618	2.43	1.00	0.85575	1.82	1.17
		271.5	7	0.13391	1.64	0.64	0.82644	1.63	0.63	0.12079	1.75	0.63	0.85733	3.76	1.22
CO_2–C_2H_6	21	223.2	11	0.14034	0.50	1.08	0.86522	0.83	0.80	0.13600	0.49	1.17	0.87161	0.83	0.78
		263.2	11	0.13396	0.46	0.39	0.86487	0.59	0.42	0.12997	0.33	0.40	0.87427	0.61	0.41
		283.2	13	0.13252	0.56	0.24	0.86092	0.86	0.21	0.12538	0.72	0.23	0.87480	0.83	0.19
C_3H_8–CO_2	22	244.3	10	0.13467	1.49	0.45	0.86842	1.87	2.90	0.12684	1.87	2.87	0.87362	1.89	2.80
		266.5	11	0.13438	1.98	0.58	0.86451	0.43	0.69	0.13201	0.57	0.38	0.87003	0.54	0.38
CO_2–nC_4H_{10}	23	292.6	15	0.13409	1.96	2.95	0.86562	1.87	2.90	0.12684	1.87	2.87	0.87362	1.89	2.80
		344.3	13	0.14442	0.66	0.58	0.86451	0.43	0.69	0.13201	0.57	0.38	0.87003	0.54	0.38
CO_2–nC_5H_{12}	24	273.4	11	0.12527	2.63	0.31	0.87473	2.64	0.32	0.11935	2.37	0.29	0.87921	2.74	0.34
		344.3	14	0.12821	0.74	0.92	0.88037	1.00	0.88	0.11713	0.78	1.27	0.88438	0.79	1.27
		423.5	10	0.16185	0.98	2.46	0.90946	0.95	1.94	0.14077	0.54	2.11	0.89227	0.49	2.79
CO_2–nC_6H_{14}	25	313.2	10	0.13241	2.11	0.21	0.86881	2.11	0.23	0.12283	2.11	0.34	0.87717	2.11	0.33
		353.2	14	0.13722	2.60	0.39	0.87336	3.07	0.57	0.12677	2.54	0.72	0.87609	2.63	0.73
		393.2	15	0.14564	1.70	0.94	0.89088	2.56	1.09	0.12717	1.36	0.91	0.88664	1.69	0.98
CO_2–benzene	26	298.2	8	0.07611	1.99	0.14	0.92291	1.95	0.13	0.07737	1.93	0.10	0.92291	1.98	0.12
		313.2	9	0.07906	1.80	0.35	0.92176	1.84	0.33	0.07899	1.70	0.27	0.92148	1.71	0.29
CH_4–H_2S	27	277.6	21	0.07963	3.74	1.12	0.89274	5.68	1.17	0.08176	3.72	1.46	0.86642	3.67	1.60
		310.9	20	0.10447	2.59	1.25	0.83085	2.34	1.17	0.10094	2.65	1.31	0.81808	2.31	0.84
		344.3	7	0.13079	0.74	2.11	0.76601	0.27	1.50	0.15734	2.44	1.46	0.76119	0.28	1.71
C_2H_6–H_2S	28	227.9	7	0.08992	0.61	1.68	0.91799	0.41	3.16	0.08649	0.71	1.99	0.92163	0.36	3.22
		255.3	8	0.08720	0.33	1.79	0.91107	0.49	2.21	0.08735	0.43	1.90	0.91556	0.47	2.27
		283.2	14	0.08416	0.53	1.34	0.91194	0.58	1.18	0.08254	0.54	1.34	0.91260	0.56	1.25
H_2S–C_3H_8	29	(260.9–327.6)	15	0.08422	1.38	1.36	0.91003	1.73	1.21	0.08039	1.54	1.28	0.91689	1.67	1.24
H_2S–nC_5H_{12}	30	310.9	7	0.05561	0.68	0.88	0.93988	0.23	0.89	0.04949	0.44	0.80	0.94788	0.25	0.84
		377.6	12	0.08214	0.82	1.44	0.91706	1.13	1.65	0.07243	1.19	1.80	0.92804	1.18	1.79
		410.9	11	0.11447	3.37	2.45	0.89988	2.09	1.81	0.09449	3.38	3.23	0.90620	3.18	3.03
Average					1.55	1.07		1.69	1.08		1.58	1.16		1.63	1.23

TABLE 3

Comparison of the deviations (eqns. (1, 2)) in bubble point calculations using the RKS, FRKS, PR and FPR methods for CO_2–polar and polar–polar binary systems

System	Ref.	T (K)	N	RKS			FRKS			PR			FPR		
				k_{12}	ΔP (%)	Δy_1	L_{12}	ΔP (%)	Δy_1	k_{12}	ΔP (%)	Δy_1	L_{12}	ΔP (%)	Δy_1
CO_2–methanol	26	298.2	8	0.02356	7.95	0.11	0.96104	5.59	0.06	0.04307	5.55	0.06	0.95577	5.64	0.06
		313.2	9	0.02356	15.62	0.42	0.94123	3.72	0.21	0.02356	18.77	0.55	0.95043	8.14	0.33
Acetone–CO_2	31	298.2	13	0.00222	0.77	0.24	0.99701	0.83	0.18	0.00523	0.86	0.17	0.99438	0.93	0.16
		313.2	12	0.00973	0.47	0.28	0.99031	0.49	0.16	0.01245	0.50	0.18	0.98667	0.52	0.12
Acetone–methanol	32	373.2	14	−0.00591	1.95	0.96	1.01667	2.20	2.11	−0.00353	1.93	0.91	1.01768	2.23	2.11
		423.2	15	0.00189	1.84	2.10	1.00514	1.23	2.45	0.00514	1.91	1.90	1.00600	1.26	2.45
		473.2	10	0.00027	2.72	3.38	0.99979	1.42	3.49	0.00237	2.65	3.26	1.00112	1.38	3.51
Acetone–H_2O	32	423.2	17	−0.18577	7.51	3.52	1.19510	6.21	3.52	−0.18299	8.18	3.47	1.19421	6.21	3.51
		473.2	25	−0.15146	6.34	2.82	1.15866	5.73	2.85	−0.14970	6.60	2.85	1.15862	5.72	2.84
		523.2	17	−0.08544	4.90	3.23	1.07935	5.01	3.32	−0.08864	4.66	3.14	1.08394	4.98	3.31
Methanol–H_2O	32	423.2	14	−0.08032	1.99	1.64	1.07260	0.79	1.09	−0.07759	1.48	1.46	1.07185	0.84	1.05
		473.2	15	−0.07726	1.15	0.93	1.06919	0.66	1.04	−0.07214	0.92	0.95	1.06726	0.67	0.98
		523.2	12	−0.07192	1.05	1.24	1.07185	0.91	1.16	−0.06855	1.02	1.21	1.07070	1.02	1.13
Ethanol–H_2O	33	473.2	17	−0.08897	1.96	1.55	1.08695	1.95	1.60	−0.08677	2.13	1.65	1.08742	1.29	1.61
		523.2	18	−0.07540	2.58	1.35	1.07307	2.39	1.19	−0.07389	2.36	1.26	1.07249	2.29	1.20
		573.2	9	−0.07192	1.70	0.95	1.06524	1.25	0.83	−0.07598	1.32	0.87	1.06496	1.20	0.82
NH_3–H_2O	34	353.2	8	−0.27910	7.37	3.38	1.26767	2.36	2.07	−0.26767	7.80	2.13	1.26767	6.79	2.62
		370.2	7	−0.29082	4.03	2.65	1.28125	2.94	1.62	−0.27090	3.44	2.13	1.26767	3.06	1.54
		400.2	6	−0.27951	4.23	2.43	1.27495	2.93	2.08	−0.25738	3.43	2.30	1.25564	2.70	2.04
Average					4.01	1.75		2.56	1.63		3.97	1.60		3.00	1.65

TABLE 4

Fixed optimum values of binary interaction parameters L_{12} and k_{12} for use in the RKS, PR, FRKS and FPR methods [a]

System	T (K) range	P (atm) range	No. of data points	k_{12}		L_{12}	
				RKS	PR	FRKS	FPR
CH_4–C_2H_6	144–200	1–51	126	−0.02404	0.0	1.02365	1.00461
CH_4–C_3H_8	277–361	6–100	99	0.02519	0.02628	0.90964	0.89873
CH_4–$n$$C_4H_{10}$	294–394	2–131	123	0.02418	0.02959	0.89099	0.87398
CH_4–$n$$C_6H_{14}$	298–423	10–120	51	0.03441	0.03790	0.88338	0.86696
CH_4–$n$$C_8H_{18}$	298–423	10–70	33	0.04571	0.04231	0.87584	0.88073
C_2H_6–C_3H_8	310–344	12–51	49	−0.00341	−0.00325	1.00121	1.00324
C_2H_6–$n$$C_5H_{12}$	277–411	0–67	66	0.00553	0.00869	1.00074	0.99285
C_2H_6–$n$$C_6H_{14}$ [b]	338–450	0–78	42	−0.02566	−0.02790	1.04331	1.03441
C_2H_6–$n$$C_8H_{18}$	313–373	4–52	46	0.01744	0.01877	0.98720	0.87327
CH_4–CO_2	209–271	14–78	42	0.10378	0.10088	0.89274	0.87312
CO_2–C_2H_6	223–293	5–62	65	0.13682	0.12757	0.86526	0.87323
C_3H_8–CO_2	244–267	5–26	21	0.13438	0.12950	0.86837	0.87520
CO_2–$n$$C_4H_{10}$ [c]	310–378	3–74	54	0.14267	0.13632	0.86371	0.86557
CO_2–$n$$C_6H_{14}$	313–393	7–114	39	0.13937	0.12717	0.87649	0.88119
H_2S–C_3H_8	217–344	1–27	41	0.08502	0.08207	0.91567	0.92101
H_2S–$n$$C_5H_{12}$	277–411	0–89	55	0.08407	0.07214	0.93192	0.93969
CO_2–methanol	298–313	5–80	17	0.02356	0.05277	0.94726	0.94297
Acetone–CO_2	298–313	4–73	25	0.00644	0.01073	0.99184	0.98838
Acetone–methanol	373–473	3–39	39	−0.00491	−0.00378	1.00653	1.00736
Acetone–H_2O	373–523	3–67	69	−0.12428	−0.12335	1.15080	1.14466
Methanol–H_2O	373–523	1–84	56	−0.08116	−0.08131	1.08022	1.07922
Ethanol–H_2O	423–623	5–187	85	−0.08528	−0.08344	1.08324	1.08266
NH_3–H_2O	333–420	0–16	63	−0.28314	−0.26532	1.27462	1.26366

[a] The data were taken from the same sources as in Tables 1–3, except for the C_2H_6–$n$$C_6H_{14}$ and CO_2–$n$$C_4H_{10}$ systems. [b] Ref. 35. [c] Ref. 36.

TABLE 5

Coefficients of function $L_{12} = e_{12} + f_{12}x_1 + g_{12}p + h_{12}T$ (eqn. (7)) for use in the F-RKS and F-PR methods

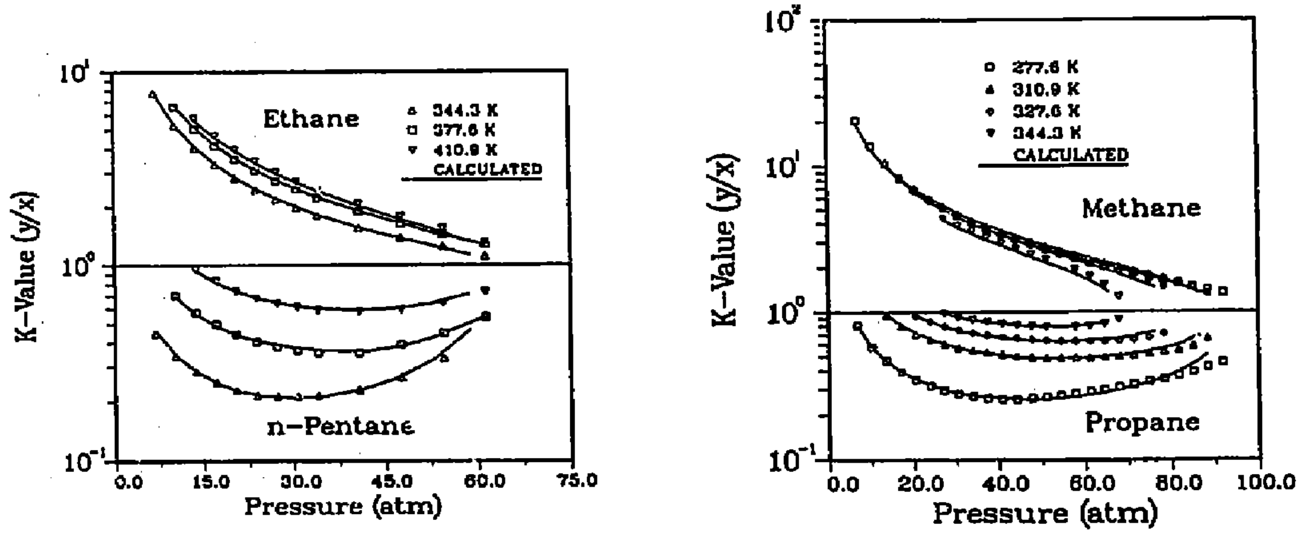
System	F-RKS				F-PR			
	e_{12}	$f_{12} \times 10$	$g_{12} \times 10^2$	$h_{12} \times 10^3$	e_{12}	$f_{12} \times 10$	$g_{12} \times 10^2$	$h_{12} \times 10^3$
CH_4–C_2H_6	0.91969	0.83496	−0.20540	0.47287	0.93107	0.81274	−0.21117	0.38543
CH_4–C_3H_8	1.04108	3.90086	−0.28337	−0.31311	1.04092	0.39431	−0.28754	−0.36162
CH_4–$n C_4H_{10}$	1.40601	1.38822	−0.08200	−1.60383	1.38279	0.57304	−0.04681	−1.58562
CH_4–$n C_6H_{14}$	1.50654	−5.78813	0.22034	−1.90599	1.32232	−0.84070	0.02649	−1.40352
CH_4–$n C_8H_{18}$	1.37259	−5.83196	0.24386	−1.55849	1.31978	−3.50149	0.15840	−1.44813
C_2H_6–C_3H_8	0.72721	0.82969	−0.25168	0.99842	1.14515	−0.23852	−0.00310	−0.41566
C_2H_6–$n C_5H_{12}$	0.98177	0.00245	−0.03250	0.06888	1.03412	−0.21499	0.00760	−0.10911
C_2H_6–$n C_6H_{14}$	1.33681	−3.09380	0.05582	−0.60808	1.38080	−3.17907	0.10711	−0.78555
C_2H_6–$n C_8H_{18}$	0.97034	−0.04394	0.00909	0.04837	0.96857	0.10874	−0.02507	0.04507
CH_4–CO_2	1.06985	−0.10500	−0.02997	−0.75695	1.02469	0.10645	−0.01539	−0.63041
CO_2–C_2H_6	0.82405	0.25123	−0.04192	0.14198	0.77907	0.26877	−0.07412	0.37923
C_3H_8–CO_2	0.84623	−0.61831	−0.17020	0.31914	0.84399	−0.59244	−0.19177	0.35899
CO_2–$n C_4H_{10}$	0.83952	0.45950	−0.02551	0.05316	0.83843	0.48380	−0.04484	0.09062
CO_2–$n C_6H_{14}$	0.83806	−0.15791	0.05872	0.04047	0.92289	0.03852	0.04621	−0.19589
H_2S–C_3H_8	0.95863	0.48280	−0.00182	−0.22517	0.96527	0.46668	0.03203	−0.23882
H_2S–$n C_5H_{12}$	0.89365	0.62604	−0.16704	0.12984	0.86123	0.77480	−0.21443	0.26144
CO_2–methanol	1.49264	−1.17616	0.05690	−1.73314	1.24851	−1.37582	0.09331	−0.96250
Acetone–CO_2	1.06518	0.53200	0.04847	−0.38540	1.18077	0.51239	0.07749	−0.79382
Acetone–methanol	1.18228	−0.09247	0.04964	−0.42265	1.16872	−0.06753	0.04344	−0.38812
Acetone–H_2O	1.06198	−0.47801	−0.26485	0.34327	1.04524	−0.36019	−0.26869	0.37775
Methane–H_2O	1.18198	−0.15261	0.04535	−0.25613	1.16721	−0.16432	0.02559	−0.21664
Ethanol–H_2O	1.13138	−0.36839	−0.01315	−0.07166	1.03910	−0.32886	−0.05932	0.15039
NH_3–H_2O	1.25692	1.04788	−0.11352	0.02457	1.33853	0.55256	−0.09638	−0.21381

TABLE 6

Comparison of bubble point calculations using the RKS, FRKS, F-RKS, PR, FPR and F-PR methods

System	RKS			FRKS[a]			F-RKS[b]			PR			FPR[a]			F-PR[b]		
	ΔP (%)	Δy_1	Rej.[c]	ΔP (%)	Δy_1	Rej.[c]	ΔP (%)	Δy_1	Rej.[c]	ΔP (%)	Δy_1	Rej.[c]	ΔP (%)	Δy_1	Rej.[c]	ΔP (%)	Δy_1	Rej.[c]
CH_4–C_2H_6	2.04	0.62	6	2.65	0.52	5	2.01	0.39	5	2.05	0.76	7	2.05	0.25	7	1.88	0.29	6
CH_4–C_3H_8	1.68	1.23	8	4.88	1.21	7	1.44	0.99	5	1.52	1.38	9	4.68	1.72	8	1.83	1.32	8
CH_4–nC_4H_{10}	2.62	1.86	0	6.46	1.98	0	2.05	1.63	0	2.55	1.53	0	7.39	1.84	0	2.00	1.21	0
CH_4–nC_6H_{14}	2.62	1.45	0	10.71	1.75	0	1.85	1.57	0	2.09	1.38	0	12.25	1.90	0	1.70	1.41	0
CH_4–nC_8H_{18}	2.47	0.31	0	11.79	0.62	0	1.04	0.20	0	1.95	0.38	0	14.28	0.81	0	1.23	0.29	0
C_2H_6–C_3H_8	2.20	1.18	11	1.83	1.02	9	1.33	0.78	8	2.19	1.53	10	2.05	0.78	10	2.34	1.52	10
C_2H_6–nC_5H_{12}	2.01	1.13	0	1.86	0.81	0	1.90	0.78	0	2.29	0.93	0	2.21	0.88	0	2.15	0.85	0
C_2H_6–nC_6H_{14}	11.23	2.26	0	9.79	2.22	0	3.96	2.08	0	11.13	2.37	0	10.59	2.18	0	4.44	2.40	0
C_2H_6–nC_8H_{18}	1.56	0.78	0	1.40	0.77	0	1.37	0.77	0	1.54	0.74	0	1.45	0.75	0	1.47	0.75	0
Average	3.16	1.20		5.71	1.21		1.88	1.02		3.03	1.22		6.33	1.23		2.12	1.12	
CH_4–CO_2	2.60	1.06	0	5.49	1.50	0	2.56	1.20	0	2.56	1.08	0	4.18	1.71	0	2.99	1.38	0
CO_2–C_2H_6	0.67	0.51	4	0.76	0.47	4	0.59	0.38	2	1.23	0.56	3	0.81	0.46	3	0.70	0.38	3
C_3H_8–CO_2	1.75	0.52	0	2.01	0.52	0	1.41	0.53	0	1.57	0.50	0	2.03	0.52	0	1.46	0.52	0
CO_2–nC_4H_{10}	2.00	1.03	0	1.48	0.84	0	0.99	0.78	0	1.82	0.97	0	1.58	0.90	0	1.37	0.85	1
CO_2–nC_6H_{14}	2.21	0.64	0	3.13	0.70	0	1.26	0.61	0	1.99	0.70	0	2.36	0.71	0	1.23	0.56	0
H_2S–C_3H_8	2.78	1.75	0	3.41	1.97	0	1.96	1.94	0	2.69	1.71	0	3.32	1.97	0	1.95	1.53	0
H_2S–nC_5H_{12}	5.01	1.87	1	3.26	1.41	1	2.05	1.68	1	4.31	1.89	1	3.22	1.61	1	2.49	2.02	0
Average	2.43	1.05		2.79	1.07		1.55	1.02		2.31	1.06		2.50	1.13		1.74	1.03	
CO_2–methanol	12.01	0.27	0	6.37	0.17	0	3.01	0.20	0	6.99	0.20	0	6.73	0.19	0	4.06	0.22	0
Acetone–CO_2	0.98	0.27	0	0.94	0.16	0	0.84	0.17	0	1.02	0.19	0	1.10	0.13	0	0.86	0.14	0
Acetone–methanol	2.02	2.14	0	2.25	2.60	0	1.82	2.66	0	2.17	2.05	0	2.26	2.59	0	1.79	2.67	0
Acetone–H_2O	5.08	3.14	0	5.95	2.92	0	3.38	2.44	0	5.12	3.28	0	5.88	2.99	0	3.40	2.48	0
Methanol–H_2O	2.22	1.80	0	1.59	1.05	0	0.95	1.01	0	2.35	1.53	0	1.81	1.05	0	0.98	0.95	0
Ethanol–H_2O	2.12	1.42	3	2.30	1.30	3	1.14	1.20	3	2.08	1.41	4	2.36	1.38	4	1.24	1.23	4
NH_3–H_2O	8.52	2.51	0	3.97	2.06	0	1.82	1.85	0	6.95	2.05	0	5.00	1.91	0	4.21	2.33	0
Average	4.71	1.65		3.34	1.47		1.85	1.36		3.81	1.53		3.59	1.46		2.36	1.43	

[a] Results obtained using fixed binary interaction parameter L_{12} (Table 4). [b] Results obtained using binary interaction parameter function $L_{12}(T, P, x_1)$. [c] Number of rejected data points including the points yielding trivial solutions and the points for which $B > Z$ (eqn. (A8)).

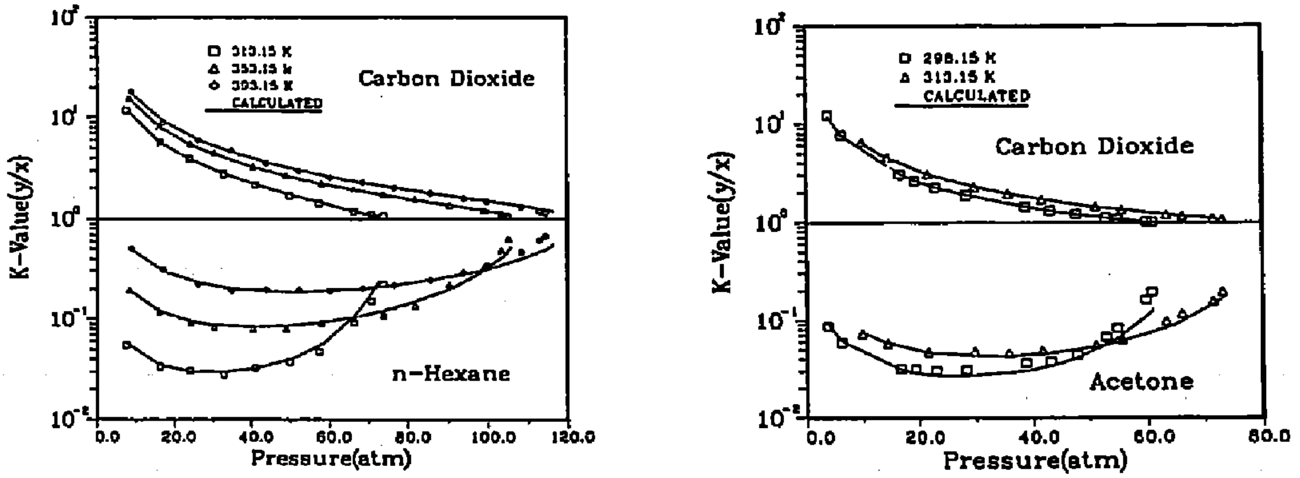


(a) (b)

Fig. 1. Comparison of calculated (F-RKS) and experimental K values for (left) ethane–n-pentane at 344.3, 377.6 and 410.9 K [17]; and (right) methane–propane at 277.6, 310.9, 327.6 and 344.3 K [10].

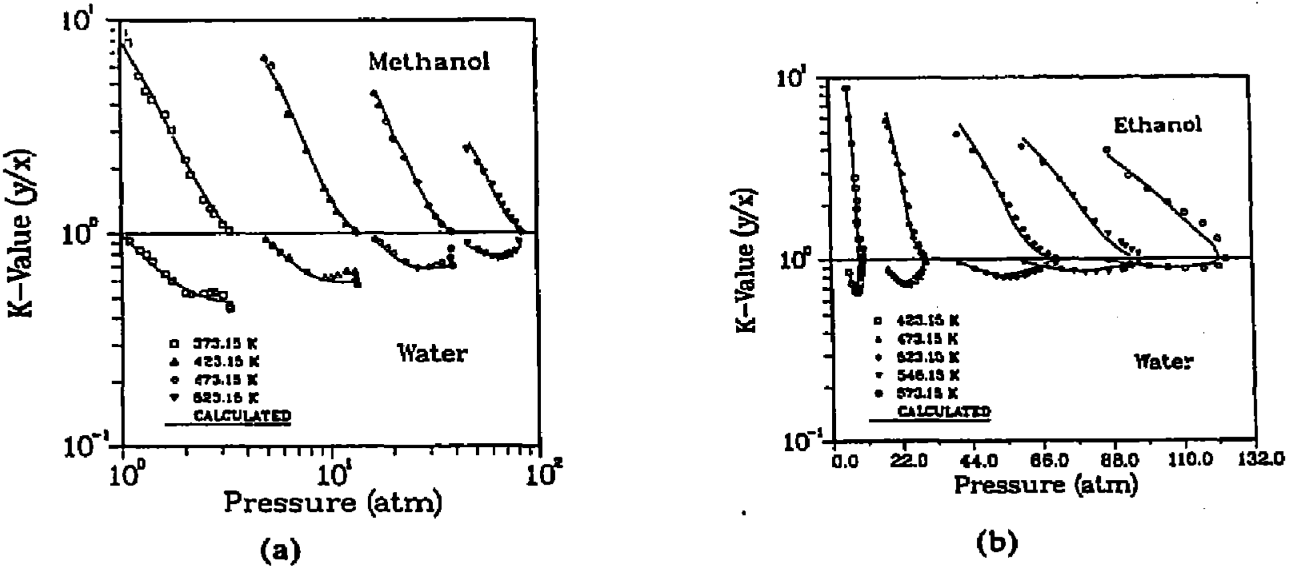
Fixed binary interaction parameter L_{ij} *values*

The fixed optimum isothermal binary interaction parameter L_{ij} values for seventy-eight isotherms of the twenty-nine binary systems were calculated from the FRKS and FRP equations by minimizing the objective function SP



(a) (b)

Fig. 2. Comparison of calculated (F-RKS) and experimental K values for (left) carbon dioxide–n-hexane at 313.15, 353.15 and 393.15 K [25]; and (right) acetone–carbon dioxide at 298.15 and 313.15 K [31].



(a) (b)

Fig. 3. Comparison of calculated (F-RKS) and experimental K values for (left) methanol–water at 373.15, 423.15, 473.15 and 523.15 K [32]; and (right) ethanol–water at 423.15, 473.15, 523.15, 548.15 and 573.15 K [33].

given as

$$SP = \frac{100}{N}\sum_{i}^{N}\left(\left|\frac{P_{cal}-P_{exp}}{P_{exp}}\right|_i + |y_{cal}-y_{exp}|_i\right) \tag{6}$$

over the same set of experimental data. The optimum k_{ij} values for the original RKS and PR equations were obtained using the same optimum search procedure. Tables 1–3 compare all the results. Table 1 shows the relative deviations of pressure ΔP (%) and absolute deviations of vapour mole-fraction Δy for eleven paraffin–paraffin compound binary systems. Table 2 compares the same (ΔP (%) and Δy) for seven CO_2–paraffin and four H_2S–paraffin compound binary mixtures. Table 3 shows the ΔP (%) and Δy comparison for seven CO_2–polar and polar–polar compound binary systems. As seen from Tables 1–3 (fixed isothermal L_{ij} and k_{ij} values) for paraffin–paraffin, CO_2–paraffin and H_2S–paraffin compound binary systems, the original RKS and PR equations of state have a slight edge over the FRKS and FPR equations. For CO_2–polar and polar–polar compound binary systems, the FRKS and FPR equations show better prediction patterns than the corresponding RKS and PR equations.

Interaction parameter function $L_{ij}(T, P, x_i)$

Following Lielmezs [6, 7] work, the binary interaction parameter function $L_{ij}(T, P, x_i)$ has been introduced into the FRKS and FPR equations, yielding the F-RKS and F-PR equations for vapour–liquid equilibrium calculations. We write the $L_{ij}(T, P, x_i)$ function as

$$L_{ij} = e_{ij} + f_{ij}x_i + g_{ij}P + h_{ij}T \tag{7}$$

where coefficients e_{ij}, f_{ij}, g_{ij} and h_{ij} are characteristic dimensionless [6, 7] constants of the given binary systems.

To satisfy the requirement that $L_{ij} = 1$ and $L_{ji} = L_{ij}$, we set

$$\begin{array}{llll} e_{ij} = 1, & f_{ii} = 0, & g_{ii} = 0, & h_{ii} = 0 \\ e_{ji} = e_{ij}, & f_{ji} = \dfrac{x_i}{x_j} f_{ij}, & g_{ji} = g_{ij}, & h_{ji} = h_{ij} \end{array} \qquad (8)$$

The coefficients e_{ij}, f_{ij}, g_{ij} and h_{ij} (eqn. (7)) for use in the F-RKS and F-PR equations were determined as follows. First, the optimum L_{ij} value (eqn. (7)) for every experimental data point of a given binary system was calculated by minimizing the objective function SP in conjunction with the F-RKS and F-PR equations (eqn. (6), $i = 1$). Those experimental data points which gave sharply fluctuating L_{ij} values were discarded, thus yielding a directional set of L_{ij} values for the given binary system. Then, from this stable set of L_{ij} values, values of the coefficients e_{ij}, f_{ij}, g_{ij} and h_{ij}, again in conjunction with the F-RKS and F-PR equations, were obtained by means of multi-property linear regression methods. The calculated values of the coefficients e_{ij}, f_{ij}, g_{ij} and h_{ij} (eqn. (7)) for the twenty-three binary systems are listed in Table 5.

To calculate the bubble-point pressure using the L_{ij}-function (eqn. (7)) for the F-RKS and F-PR equations, an initial P value is first assumed. For this initial P, using eqn. (7) an initial L_{ij} value can be obtained and the iteration process started, i.e. when the pressure P value of the first iteration has been obtained, a new L_{ij} value can be calculated from it. The iterations need to be repeated until a preset convergence limit has been reached. In this work the limit is

$$\left|1 - \sum_i y_i\right| \leq 10^{-5} \qquad |(P_n - P_{n+1})|/P_{n+1} \leq 10^{-4}$$

Table 6 presents a comparative evaluation of the bubble point calculations performed by means of the averaged optimum values of the fixed binary interaction parameters L_{ij} and k_{ij} (FRKS and FPR, and RKS and PR equations) and the binary interaction parameter L_{ij}-function (F-RKS and F-PR equations).

Table 6 shows that over narrower T and P ranges, the FRKS and FPR equations (fixed, state-independent binary interaction parameter L_{ij} values) predict vapor–liquid equilibria with reasonable accuracy. For larger T and P ranges, for instance, CH_4–$n C_4H_{10}$, CH_4–$n C_6H_{14}$, CH_4–$n C_8H_{18}$ binaries, the predictive accuracy of the FRKS and FPR equations decreases. However, the F-RKS and F-PR equations (state-dependent binary interaction parameter L_{ij}-function, eqn. (7)) predict the vapour–liquid equilibria with high accuracy for all the systems tested. Figures 1–3 confirm further the predictive superiority of the F-RKS and F-PR equations. These figures show vaporization equilibrium ratio K values plotted against the pressure P at several fixed temperatures. As seen from Figs. 1–3, the F-RKS equation predicts accurately the vapourization equilibrium ratio K values for a set of selected non-polar and polar binary systems up to their critical points.

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APPENDIX

The generalized F-function modification of the two-parameter cubic equation of state [1–3] can be written as

$$P=\frac{RT}{V-b}-\frac{\Omega_a}{\Omega_b}\frac{RTb}{V^2+ubV+wb^2}F(T_r) \tag{A1}$$

where u and w must satisfy the constaints

$$w>-u-1 \qquad \text{for } u\geq -2$$
$$w>\frac{u^2}{4} \qquad \text{for } u\leq -2 \tag{A2}$$

while

$$b=\Omega_b\frac{RT_c}{P_c} \tag{A3}$$

$$F(T_r)=\sum_{n=1}^{m} c_n T_r^{(1-n)/2} \tag{A4}$$

where T_r is reduced temperature and c_n $(n=1,2,\ldots,m)$ are empirical substance-dependent coefficients.

The compressibility factor equation is

$$Z^3+(uB-B-1)Z^2+(A+wB^2-uB-uB^2)Z$$
$$-(AB+wB^2+wB^3)=0 \tag{A5}$$

where

$$A=\frac{\Omega_a}{\Omega_b}BF \tag{A6}$$

$$B=\frac{bP}{RT} \tag{A7}$$

The generalized fugacity coefficients of component k in a mixture is

$$\ln\phi_k=\frac{b_k}{b_m}(Z-1)-\ln(Z-B)+\frac{\Omega_a}{\Omega_b}\frac{F_m}{b_m\sqrt{u^2-4w}}$$
$$\times\left[b_k-\frac{2(b_kF_k)^{1/2}\sum_i x_i(b_iF_i)^{1/2}L_{ki}}{F_m}\right]$$
$$\times\ln\left[\frac{2Z+B(u+\sqrt{u^2-4w})}{2Z+B(u-\sqrt{u^2-4w})}\right] \tag{A8}$$

The F-function modification of the Redlich–Kwong–Soave equation of state (FRKS):

$u = 1, \qquad w = 0$

$\Omega_a = 0.42748$

$\Omega_b = 0.08664$

$$Z^3 - Z^2 + (A - B - B^2)Z - AB = 0 \tag{A9}$$

$$\ln \phi_k = \frac{b_k}{b_m}(Z - 1) - \ln(Z - B) + \frac{\Omega_a}{\Omega_b}\frac{F_m}{b_m} \times \left[b_k - \frac{2(b_k F_k)^{1/2} \sum_i x_i (b_i F_i)^{1/2} L_{ki}}{F_m} \right] \times \ln\left(1 + \frac{B}{Z}\right) \tag{A10}$$

The F-function modification of the Peng–Robinson equation of state (FPR):

$u = 2, \qquad w = -1$

$\Omega_a = 0.45724$

$\Omega_b = 0.07780$

$$Z^3 + (B - 1)Z^2 + (A - 2B - 3B^2)Z - (AB - B^2 - B^3) = 0 \tag{A11}$$

$$\ln \phi_k = \frac{b_k}{b_m}(Z - 1) - \ln(Z - B) + \frac{\Omega_a}{\Omega_b}\frac{F_m}{2\sqrt{2}\, b_m} \times \left[b_k - \frac{2(b_k F_k)^{1/2} \sum x_i (b_i F_i)^{1/2} L_{ki}}{F_m} \right] \times \ln\left[\frac{Z + B(1 + \sqrt{2})}{Z + B(1 + \sqrt{2})}\right] \tag{A12}$$