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Use of F-function of two-parameter cubic equation of state in $P-V-T$ calculations of binary mixtures

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Abstract

The applicability of the recently proposed F-function of Shaw and Lielmezs and Mak and Lielmezs, modified to fit the van der Waals type cubic equation of state, has been studied over a wide range of $P-V-T-x$ values by means of available gas and liquid state experimental data for pure substances and binary mixtures. New optimum binary interaction parameters $L_{ij} = L_{ij}(T, P, x)$, functionally dependent on temperature (T), pressure (P) and composition (x), were introduced for 18 selected binary mixtures. The predicted (this work) saturated vapour pressure and liquid and vapour volume values for pure substance and liquid and vapour compressibility factor values for binary systems are in excellent agreement with the experimental data, and show a slight edge over the values calculated by means of the original Redlich–Kwong–Soave (RKS) and Peng–Robinson (PR) equations.

LIST OF SYMBOLS

a, b	parameter of cubic equation of state
A, B	dimensionless parameters
C_1, C_2, C_3, C_4, C_5	coefficients of eqn. (4)
e, f, g, h	dimensionless coefficients of eqn. (8)
F	F-function
k_{ij}	binary interaction parameter
L_{ij}	binary interaction parameter
P	pressure
R	universal gas constant
RMS	root mean square
T	temperature
V	volume

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x	composition, mole fraction
Z	compressibility factor
Ω_a, Ω_b	constants of eqn. (1)

Subscripts

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

INTRODUCTION

Following the suggestions of Schmidt and Wenzel [1] and Shaw and Lielmezs [2], Mak and Lielmezs [3] have proposed that the generalized two-parameter cubic equation of state can be expressed as

$$P = \frac{RT}{V-b} - \frac{\Omega_a}{\Omega_b} \frac{RTb}{V^2 + ubV + wb^2} F(T_r) \tag{1}$$

where u and w must satisfy the constraints [1]

$$\begin{aligned} &w > -u - 1 \qquad \text{for } u \geqslant -2 \\ &w > u^2/4 \qquad \text{for } u \leqslant -2 \end{aligned} \tag{2}$$

while

$$b = \Omega_b \frac{RT_c}{Pc} \tag{3}$$

and

$$F(T_r) = \sum_{n=1}^{m} C_n T_r^{(1-n)/2} \tag{4}$$

where T_r is the reduced temperature and C_n ($n = 1, 2, \ldots, m$) are empirical substance-dependent coefficients determined by curve-fitting the experimental saturated vapour pressure data.

The compressibility factor of eqn. (1) is

$$Z^3 + (uB - B - 1)Z^2 + (A + wB^2 - uB - uB^2)Z - (AB + wB^2 + wB^3) = 0 \tag{5}$$

where

$$A = \frac{\Omega_a}{\Omega_b} BF \tag{6}$$

$$B = \frac{bP}{RT} \tag{7}$$

Mak and Lielmezs [3], using the F-function of the Redlich–Kwong–Soave equation [4] (FRKS, eqn. (1), $u = 1$, $w = 0$) and the F-function of the Peng–Robinson equation [5] (FPR, eqn. (1), $u = 2$, $w = -1$), showed that equations modified by the F-function (FRKS, FPR) gave consistently improved predictions over the original Redlich–Kwong–Soave (RKS [4]) and Peng–Robinson (PR, [5]) equations of state in saturated vapour pressure, liquid volume, enthalpy and entropy of vaporization for all pure substances considered.

To test the predictive accuracy of F-function modified Redlich–Kwong–Soave and Peng–Robinson equations further, seventeen pure substances were selected, and following the work of Mak and Lielmezs [3], empirical coefficient C_n sets (eqn. (4)) for all these compounds were determined. The results obtained (saturated vapour pressure, vapour and liquid volumes) showed a slight edge of superiority of the modified FRKS and FPR methods over the calculations performed by the original Redlich–Kwong–Soave and Peng–Robinson equations.

The applicability of the modified F-function FRKS and FPR equations in PVT calculations for binary systems was tested in two ways: first, by means of a new mixing rule which contains a fixed optimum binary interaction parameter L_{ij} independent of thermodynamic state parameters T, P and x, where $L_{ij} = 1 - k_{ij}$, and k_{ij} is the conventional binary interaction parameter [6], and, secondly, following the work of Lielmezs [6] on the Benedict–Webb–Rubin (BWR) and Starling (S) equations, by introducing, instead of the fixed optimum interaction parameter L_{ij}, a binary interaction function of state, $L_{ij}(T, P, x)$ defined as

$$L_{ij} = e + fx + gP + hT \tag{8}$$

The e, f, g and h in eqn. (8) are characteristic dimensionless [6] constants of the given binary system.

RESULTS AND DISCUSSION

Pure substances

The summary of experimental data and physical constants for all pure substances studied is given in Table 1. It is assumed that the data presented were of sufficient reliability, so that further evaluation of their accuracy was not made. The F-functions (eqn. (4)) for FRKS and FPR equations were determined by methods already outlined by Mak and Lielmezs [3]. Table 2 lists the calculated values for coefficient C_n sets (eqn. (4)) for all substances studied. The coefficient C_n values for ethane, butane and n-pentane, in this work, differ slightly from those found in ref. 3 because more experimental data points have been used.

TABLE 1

Summary of data used

Compound	Experimental data		Data source	Physical properties[a]		
	T_r range	No. of data points		P_c (atm)	T_c (K)	Pitzer acentric factor ω
Methane	0.476–0.976	50	8	45.35	190.56	0.011
Ethane	0.491–0.999	27	9, 10	48.07	305.4	0.099
Propane	0.625–0.995	23	11	41.94	369.8	0.153
n-Butane	0.641–0.992	28	12	37.47	425.2	0.199
n-Pentane	0.658–0.999	27	13	33.3	469.65	0.251
n-Hexane	0.538–0.991	33	9, 14	29.71	507.5	0.299
n-Octane	0.450–0.956	37	15	24.57	568.8	0.398
Benzene	0.498–0.998	46	9	48.26	562.3	0.212
Hydrogen	0.424–0.985	22	9	12.49	33.0	−0.216
Nitrogen	0.500–0.998	65	16	33.46	126.2	0.039
Carbon dioxide	0.712–0.999	47	17	72.83	304.1	0.239
Hydrogen sulphide	0.758–0.997	20	18, 19	88.23	373.2	0.081
Methanol	0.429–0.969	38	15	79.84	512.6	0.556
Ethanol	0.449–0.979	35	15	60.6	513.9	0.644
Acetone	0.498–0.970	33	15	46.39	508.1	0.304
Water	0.422–0.998	49	9	218.31	647.3	0.344
Ammonia	0.493–0.986	21	9	112.02	405.5	0.250

[a] Physical properties taken from Reid et al. [8].

TABLE 2

Values of coefficients C_n, $n = 1, 2, \ldots, 5$

Compound	FRKS				
	C_1	C_2	C_3	C_4	C_5
Methane	1.9674255	−5.73126842	5.73271560	−0.96891973	
Ethane	−1.08865887	1.55548556	−0.20899368	0.74216698	
Propane	−3.71874409	8.57060274	−6.57582849	2.72396984	
n-Butane	−3.34188080	7.55894258	−5.80316327	2.58610150	
n-Pentane	−4.15225480	9.50240362	−7.47004170	3.11989287	
n-Hexane	−2.13533573	4.02795962	−2.6622501	1.77360113	
n-Octane	−13.78590895	43.58554392	−53.11583382	30.23711436	−5.92091550
Benzene	−0.73968011	0.68613074	0.18937669	0.86417268	
Hydrogen	−0.74601624	1.11242460	0.63358081	0.0001083	
Nitrogen	−0.97361600	1.47306786	−0.17392863	0.67447677	
Carbon dioxide	−5.76332640	14.57959560	−12.63104838	4.81477918	
Hydrogen sulfide	1.73944705	−6.84754582	8.12143621	−2.01333744	
Methanol	1.53886397	−6.66255832	7.43767870	−1.02319542	
Ethanol	4.82942663	−14.82100424	13.31732884	−2.32575123	
Acetone	37.31272698	−124.40879029	153.15013670	−81.73058666	16.67651327
Water	−0.60598802	−0.56009157	1.75224137	0.41383823	
Ammonia	−1.76299388	2.74638835	−1.15130082	1.16790634	

Following the method of analysis of Mak and Lielmezs [3], it was found that, in order to describe the F-function (eqn. (4)) accurately, four coefficients, C_1–C_4, were needed for lower molecular weight compounds and five coefficients, C_1–C_5, were needed for higher molecular weight compounds such as n-octane and acetone.

The results of the testing were evaluated by comparing the saturated vapour pressure and saturated liquid and vapour volumes calculated via the FRKS and FPR equations and the original RKS and PR equations of state with the experimental data over the entire available data set by means of the root mean square (RMS) percentage error

$$\text{RMS\%} = \left[\frac{1}{N}\sum_i^N (\%\ \text{error})_i^2\right]^{1/2} \tag{9}$$

where

$$\%\text{error} = \left(\frac{\text{calc}_i - \text{exp}_i}{\text{exp}_i}\right) \times 100 \tag{10}$$

and calc_i = calculated value; exp_i = experimental value. Table 3 presents a summary of the obtained RMS% error distribution for all compounds and calculation methods used. Figures 1 and 2 show % error (eqn. (10)) versus T_r curves of saturated vapour pressures and vapour volumes for methane, n-octane, ethanol and water. Table 3 and Figs. 1 and 2 indicate that the F-function modification of the two-parameter cubic equation (FRKS, FPR) gives in general a better representation of saturated vapour pressure, especially in the lower temperature range (Figs. 1 and 2).

In the case of the polar compounds methanol, ethanol, water and acetone, the FRKS and FPR equations accurately predict saturated vapour pressure and vapour volume whereas the original RKS and PR

FPR

C_1	C_2	C_3	C_4	C_5
2.29187586	−6.22835561	6.00143802	−1.06495826	
−0.42376144	0.23242612	0.73481287	0.45652245	
−2.54332018	5.88750270	−4.41918891	2.07500638	
−2.09487827	4.68673338	−3.47193131	1.88007620	
−2.71204710	6.13066523	−4.70101651	2.28239839	
−1.15000227	1.89840757	−1.01518997	1.26678468	
−10.63562960	34.09005309	−42.08242875	24.43861269	−4.81060743
0.00698066	−0.84355260	1.32666495	0.50990699	
0.0	0.0	1.0	0.0	
−0.34395130	0.21937387	0.71955070	0.40502673	
−4.13850010	10.63856579	−9.28957010	3.78950442	
2.71252054	−8.97306266	9.75247591	−2.49193380	
2.11955847	−7.91341728	8.01869343	−1.22483462	
5.26811727	−15.45319026	13.67127971	−2.48620672	
36.35354354	−120.44373583	147.72590786	−78.63441721	15.99870164
0.00233628	−1.66255832	2.47286527	0.17745678	
−0.93268361	1.00496649	0.09984121	0.78787581	

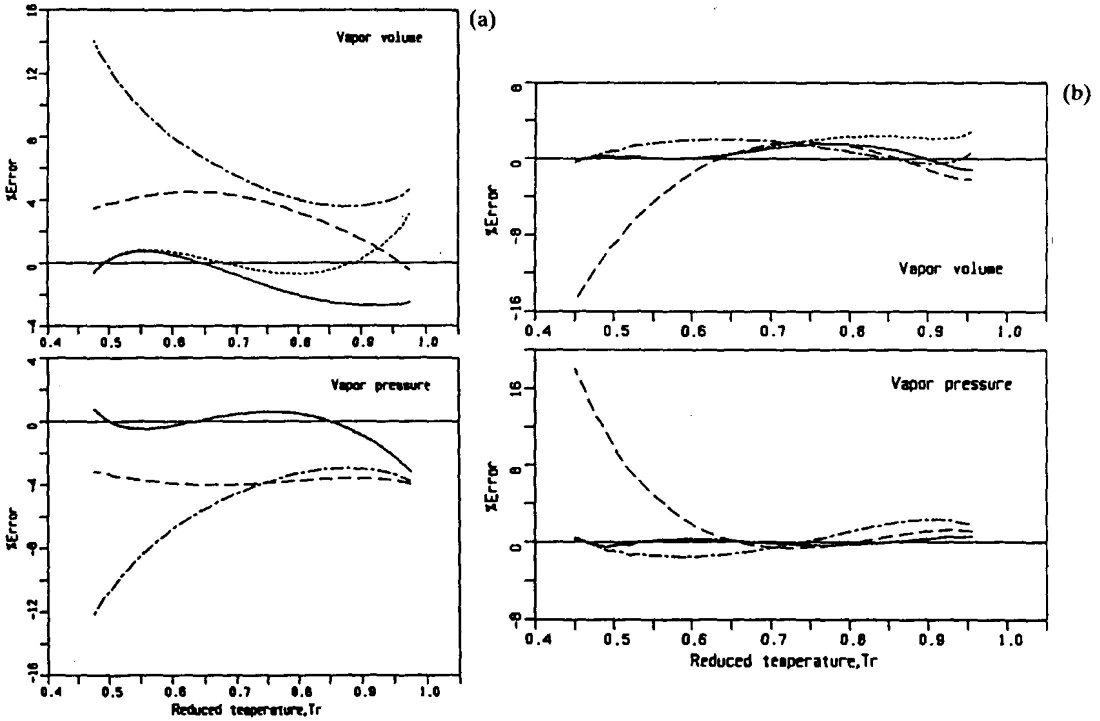

Fig. 1. % Error (eqn. (10)) vs T_r curve for (a) methane; (b) octane. Key: ——, FPR; · · · , FRKS; – – – – , PR; – · – · –, RKS.

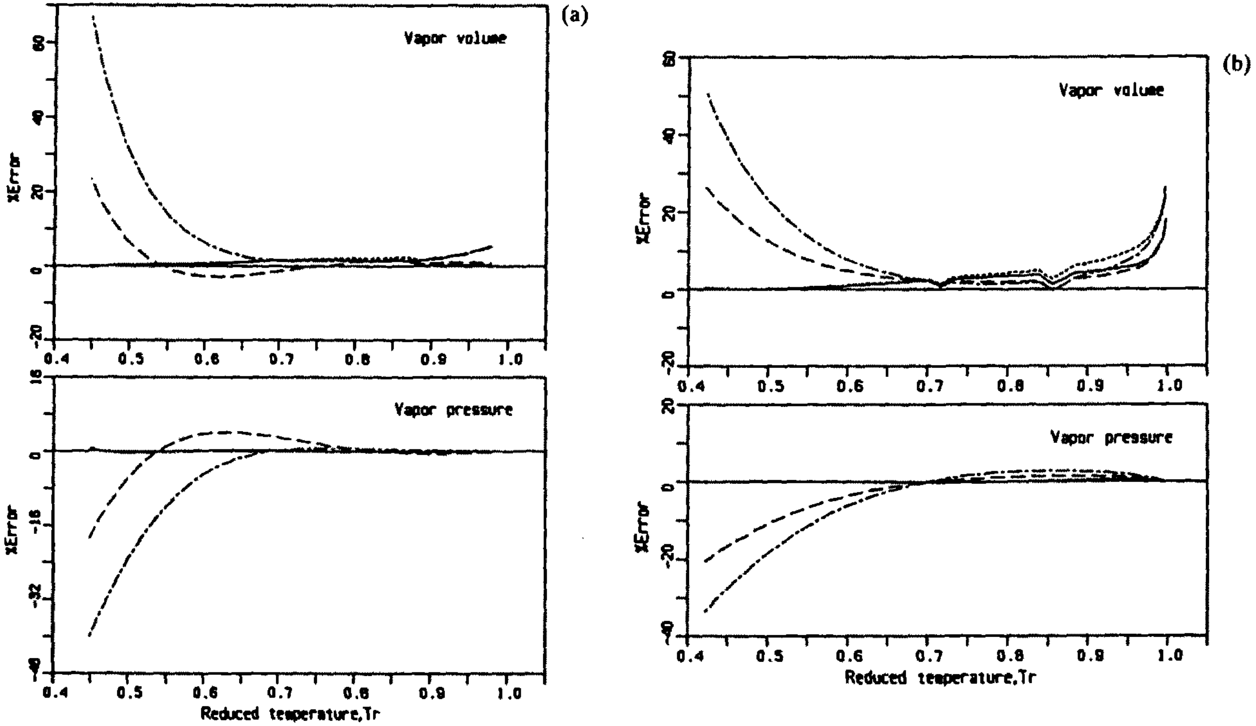

Fig. 2. % Error (eqn. (10)) vs T_r curve for (a) ethanol; (b) water. Key: ——, FPR, · · · , FRKS; – – – –, PR; – · – · –, RKS.

TABLE 3

Comparison of results for pure compounds

Compound	RMS% error											
	Pressure				Liquid vol.				Vapour vol.			
			This work				This work				This work	
	RKS	PR	FRKS	FPR	RKS	PR	FRKS	FPR	RKS	PR	FRKS	FPR
Methane	6.01	3.75	0.91	0.92	11.09	6.02	11.88	6.15	7.04	3.49	0.85	1.68
Ethane	2.05	0.70	0.59	0.59	17.00	9.50	16.70	9.45	3.39	1.91	3.23	1.70
Propane	0.85	0.32	0.11	0.10	19.87	10.58	18.74	10.39	2.49	1.93	2.79	1.56
n-Butane	0.68	0.24	0.08	0.07	22.41	12.00	20.29	11.87	5.07	2.33	3.28	2.27
n-Pentane	1.13	0.42	0.14	0.13	24.09	13.55	23.46	13.30	4.73	1.36	5.57	1.52
n-Hexane	1.31	0.90	0.26	0.24	17.31	6.45	17.01	6.37	3.46	3.24	3.69	3.04
n-Octane	1.41	5.36	0.31	0.29	18.47	5.55	18.20	5.39	1.28	4.83	1.57	0.86
Benzene	0.87	1.73	0.42	0.38	18.29	8.30	18.21	8.40	4.66	6.48	4.43	6.76
Hydrogen	10.43	4.98	0.15	4.98	10.05	14.00	9.42	14.00	14.47	7.78	1.14	7.78
Nitrogen	1.82	0.80	0.13	0.10	7.93	9.33	7.76	9.33	2.38	2.14	1.13	2.03
Carbon dioxide	1.57	2.31	0.09	0.08	16.44	7.21	16.44	7.24	4.18	3.44	3.24	1.16
Hydrogen sulphide	1.47	0.82	0.20	0.20	16.11	6.14	15.38	5.99	2.72	1.81	3.71	1.11
Methanol	21.94	16.05	0.83	0.85	36.90	21.61	36.67	21.39	45.22	26.96	1.69	1.04
Ethanol	12.37	4.93	0.14	0.23	25.55	12.18	25.59	12.27	18.38	5.56	2.05	1.04
Acetone	8.27	6.91	1.02	1.02	40.12	24.13	41.54	25.68	11.86	9.84	3.07	2.79
Water	13.11	7.85	0.28	0.20	41.41	26.40	41.14	26.25	19.51	10.76	8.53	5.53
Ammonia	2.94	2.13	0.58	0.54	28.54	14.29	27.54	13.90	5.77	3.81	7.33	5.23
Average	5.18	3.54	0.36	0.64	21.85	12.19	21.52	12.19	9.21	5.75	3.37	2.77

equations fail. For hydrogen, FRKS gives better results than the original RKS and PR equations. Saturated liquid volumes of pure substances are predicted with nearly the same accuracy by all equations of state studied (Table 3).

Binary mixtures

The applicability of FRKS and FPR equations for binary mixtures was tested via the liquid and vapour state compressibility factor calculations.

Experimental data for eighteen binary systems were selected from a number of sources (Table 4). These literature data were considered to be sufficiently reliable; therefore no further evaluation of their accuracy was made. However, the few printing errors found in refs. 30 and 35 were corrected.

To extend the already established F-function modification of cubic equations of state for a pure substance (eqns. (1) and (5), this work) to binary systems, the following mixing rules are proposed

$$F_m = \frac{1}{b_m} \sum_i \sum_j x_i x_j (b_i b_j F_i F_j)^{1/2} L_{ij} \tag{11}$$

TABLE 4

Optimum fixed values of binary interaction parameters L_{12} and k_{12}

System	T range (K)	P range (atm)	x range (mol %) (1st component)	No of data pts.	Source of data used	k_{12}		L_{12}	
						RKS	PR	FRKS	FPR
CH_4–C_3H_8	311–361	12–92	0.00–0.60	70	20	−0.18319	0.00339	1.04181	0.85987
CH_4–n-C_4H_{10}	294–394	2–131	0.00–0.77	124	21	−0.23577	0.04173	1.06373	0.79710
CH_4–n-C_5H_{12}	310–344	1–167	0.00–0.82	66	22	−0.28786	0.07217	1.04003	0.71181
CH_4–n-C_6H_{14}	298–423	20–70	0.03–0.31	31	23	−0.80	−0.19915	1.80	0.96927
CH_4–n-C_8H_{18}	298–423	20–270	0.03–0.80	35	24	−0.80	−0.03814	1.80	0.87617
C_2H_6–n-C_5H_{12}	277–444	0.3–27	0.00–1.00	74	25	−0.25665	−0.02081	1.26851	1.02517
C_2H_6–n-C_6H_{18}	273–373	4–52	0.05–0.98	64	26	−0.80	−0.01589	1.80	1.00822
C_3H_6–n-C_8H_{14}	324–487	10–49	0.22–0.92	58	27	−0.15115	−0.02458	1.16380	1.03428
C_3H_8–n-C_8H_{18}	329–543	7–58	0.21–0.96	86	28	−0.22897	−0.04353	1.27137	1.06598
n-C_4H_{10}–n-C_5H_{12}	371–464	10–37	0.14–0.87	48	29	−0.20244	−0.05036	1.19556	1.04847
n-C_4H_{10}–n-C_6H_{14}	375–501	6–38	0.10–0.90	105	29	−0.31683	−0.07963	1.31277	1.07929
n-C_4H_{10}–n-C_8H_{18}	339–550	7–43	0.18–0.95	65	28	−0.23358	−0.05684	1.24215	1.06158
CH_4–CO_2	253–288	62–84	0.04–0.44	11	30	0.00907	0.11622	0.94256	0.83437
C_3H_8–CO_2	277–344	5–68	0.00–1.00	78	31	−0.02401	0.08944	1.01905	0.90833
CH_4–H_2S	277–344	12–133	0.00–0.55	62	32	−0.03226	0.15641	0.92016	0.73434
C_2H_6–H_2S	273–358	17–81	0.11–0.89	53	33	−0.05932	0.04489	1.05278	0.94588
C_3H_8–H_2S	277–366	8–78	0.10–0.84	115	34	−0.09283	0.03063	1.08076	0.96552
CH_2S–n-C_5H_{12}	277–444	0.3–88	0.00–1.00	65	35	−0.18906	−0.00820	1.18591	1.03383

TABLE 5

Coefficients of function $L_{ij} = e + fx + gP + hT$ (eqn. (8))

System	FRKS				FPR			
	e	f	$g \times 10^2$	$h \times 10^2$	e	f	$g \times 10^2$	$h \times 10^2$
CH_4–C_3H_8	4.98804	−1.58238	−0.22742	−0.97724	1.19869	−0.43930	0.33425	−0.13081
CH_4–n-C_4H_{10}	3.06054	−1.75880	0.18903	−0.37614	0.87739	−0.55027	0.30580	−0.03827
CH_4–n-C_5H_{12}	3.14529	−3.66309	1.17956	−0.40675	0.71674	−0.71160	0.34411	−0.11548
CH_4–n-C_6H_{14}	1.80	0.0	0.0	0.0	−1.25166	6.02155	−2.34744	0.61664
CH_4–n-C_8H_{18}	1.51038	2.24167	−0.85950	0.08507	1.98946	2.47596	−1.18184	−0.03734
C_2H_6–n-C_5H_{12}	1.32740	−0.05908	−1.13449	0.15447	0.53533	0.04923	−0.13057	0.14526
C_2H_6–n-C_8H_{18}	2.15622	−0.53706	0.08599	−0.06462	1.24245	−0.26045	0.15858	−0.03176
C_3H_8–n-C_6H_{14}	−0.35183	0.72459	−0.02274	0.47514	0.86956	0.05165	−0.04469	0.03585
C_3H_8–n-C_8H_{18}	1.59921	−0.11187	−1.46768	0.10054	1.01686	−0.08512	−0.17303	0.04416
n-C_4H_{10}–n-C_5H_{12}	−3.03690	0.63516	−5.00023	1.25088	−1.58964	0.33938	−1.86780	0.70005
n-C_4H_{10}–n-C_6H_{14}	−2.73950	1.07118	−5.15814	1.10905	−2.30155	0.78744	−2.84725	0.84557
n-C_4H_{10}–n-C_8H_{18}	0.22076	0.46938	−3.15775	0.38873	0.54127	0.08126	−0.31885	0.12558
CH_4–CO_2	2.36363	0.06935	−2.52413	0.21805	0.94781	0.07542	−0.45857	0.85550
C_3H_8–CO_2	−0.22354	−0.63793	−2.07375	0.85925	−0.66170	−0.64062	−0.97722	0.75995
CH_4–H_2S	1.03677	0.59920	−1.18600	0.36204	−0.99932	0.84548	−0.02357	0.48605
C_2H_6–H_2S	−3.22584	0.32874	−2.51572	1.72708	−0.10020	0.19086	−0.27911	0.34532
C_3H_8–H_2S	0.84355	−1.12780	−1.12830	0.24261	0.81685	−0.00862	−0.04230	0.04983
H_2S–n-C_5H_{12}	1.36208	0.00395	−0.61517	0.06855	0.91600	0.01685	−0.01598	0.02857

where

$$b_m = \sum_i x_i b_i \tag{12}$$

For RKS and PR equations of state we use the original mixing rules such that

$$a_m = \sum_i \sum_j x_i x_j (a_i a_j)^{1/2}(1 - k_{ij}) \tag{13}$$

and b_m is the same as in eqn. (12). The binary interaction parameter L_{ij} of eqn. (11) can be related to eqn. (13) by setting $L_{ij} = 1 - k_{ij}$. We note that for similar molecules, identified as $i = j$, $k_{ii} = 0$; yielding $L_{ii} = 1.0$. For dissimilar molecules, $i \neq j$, so that $k_{ij} \neq 0$, $L_{ij} \neq 1.0$.

Binary interaction parameter L_{ij}

Following Lielmezs [6, 7], the predictive accuracy of the binary interaction coefficient L_{ij} was tested in two ways: first, using the optimum fixed value of L_{ij} for a given binary mixture and, secondly, in place of the optimized fixed interaction parameter L_{ij} value, introducing a new binary interaction parameter function $L_{ij}(T, P, x)$ such that $L_{ij} = e + fx + gP + hT$ (eqn. (8)). The values of coefficients e, f, g and h are listed in Table 5.

Fixed binary interaction parameter L_{ij} *values*

The optimum set of fixed binary interaction parameter L_{ij} values was that set of L_{ij} values which yielded the lowest RMS% error of liquid and/or vapour compressibility factor values over the same set of experimental data. The optimum L_{ij} values were determined by means of the Fibonacci search technique [37]. The L_{ij} search range values were set between limits of $L_{ij_{\min}} = 0.3$ and $L_{ij_{\max}} = 1.8$. When a calculated L_{ij} value fell between these L_{ij} value limits, the calculation was considered to be convergent. In the case of the FRKS equation, calculations did not converge for CH_4–n-C_6H_{14}, CH_4–n-C_8H_{18} and C_2H_6–n-C_8H_{18} binary systems with their relatively large differences in molecular weight between the individual components. For the remaining 15 systems with the FRKS equation and for all the selected 18 binary systems calculated via the FPR equation of state, the results did converge. For all systems for which calculations did converge, the optimum fixed binary interaction parameter L_{ij} values were found to be close to unity.

Table 4 lists all calculated (FRKS, FPR, RKS, PR equations) optimum fixed values of the binary interaction parameter L_{ij} and of k_{ij} estimated using the same optimum search procedure.

Table 6 compares the RMS% errors in liquid and vapour compres-

TABLE 6

Comparison of RMS% error in compressibility factor calculation for saturated binary systems

System					This work					
	RKS		PR		FRKS[a]		FPR[a]		F-RKS[b]	F-PR[b]
	Liquid	Vapour	Liquid	Vapour	Liquid	Vapour	Liquid	Vapour	Liquid	Liquid
CH_4–C_3H_8	10.05	8.02	2.74	3.81	9.89	8.83	2.83	4.04	7.83	2.72
CH_4–n-C_4H_{10}	8.18	6.98	2.56	3.44	8.20	9.09	2.23	4.57	6.25	2.13
CH_4–n-C_5H_{12}	9.94	5.48	3.02	1.48	9.97	7.60	2.89	3.79	8.43	2.67
CH_4–n-C_6H_{14}	10.55	12.73	1.30	11.43	9.63	17.46	1.00	13.07	9.63	0.63
CH_4–n-C_8H_{18}	14.08	2.21	3.05	1.85	13.73	4.66	2.91	4.99	13.64	1.54
C_2H_6–n-C_5H_{12}	10.12	12.72	4.11	2.92	9.77	10.76	4.07	3.02	7.58	3.49
C_2H_6–n-C_8H_{18}	9.45		2.06		9.49		1.98		9.08	1.78
C_3H_8–n-C_6H_{14}	7.07		3.00		6.52		2.91		2.82	2.85
C_3H_8–n-C_8H_{18}	9.75		4.87		9.42		4.96		6.33	4.46
n-C_4H_{10}–n-C_5H_{12}	8.68		4.11		8.40		3.93		4.00	3.28
n-C_4H_{10}–n-C_6H_{14}	8.83		4.85		8.61		4.69		4.73	3.11
n-C_4H_{10}–n-C_8H_{18}	9.26		4.64		9.01		4.57		4.11	3.86
CH_4–CO_2	9.77		4.21		9.84		4.38		5.60	3.25
C_3H_8–CO_2	9.66	25.18	4.07	7.92	9.37	24.80	4.04	7.77	6.86	3.73
CH_4–H_2S	6.45	5.22	5.00	6.06	6.01	5.32	4.45	4.85	5.02	3.26
C_2H_6–H_2S	6.34		4.03		6.18		3.75		3.73	3.19
C_3H_8–H_2S	9.44		4.55		9.27		4.38		8.50	4.43
H_2S–n-C_5H_{12}	10.52	25.71	6.52	18.71	10.18	25.08	5.25	12.81	8.87	5.27
Average	9.34	11.58	3.82	6.40	9.08	12.62	3.62	6.55	6.83	3.09

[a] Fixed optimum binary interaction parameter L_{ij}.

[b] Binary interaction parameter function $L_{ij}(T, P, x)$ (eqn. (8)).

sibility factors calculated for binary mixtures by means of liquid state optimum fixed L_{ij} or k_{ij} values (Table 4) via the FRKS, FPR, RKS and PR equations of state. It is seen that, for liquid state compressibility factor calculations using the liquid state optimum fixed L_{ij} or k_{ij} values, the FRKS and FPR equations give values having a slight edge over the results obtained via the original RKS or PR equations of state. Table 6 also shows that the same fixed binary interaction parameters L_{ij} or k_{ij} determined from liquid state data can be used to estimate with reasonable accuracy the vapour state binary system compressibility factor values.

Table 7 and Figs 3 and 4 compare the estimated RMS% and % error in liquid and vapour compressibility factors for nine saturated binary systems obtained by determining the binary fixed interaction parameter L_{ij} and k_{ij} values via the FRKS, FPR, RKS and PR equations by minimizing the RMS% error of the calculated, saturated vapour state compressibility factor. It is seen (Table 7, Fig. 3) that, for the FRKS and RKS equations, the use of these vapour state fixed optimum L_{ij} and k_{ij} values considerably increases the predictive accuracy of the saturated vapour volume estimations but, understandably, decreases the accuracy of the liquid phase predictions. Table 6 shows the opposite behaviour in predicting patterns.

TABLE 7

Comparison of RMS% error in compressibility factor calculation for saturated binary systems

System	RKS			PR			FRKS			FPR		
	k_{12}	Liquid	Vapour	k_{12}	Liquid	Vapour	L_{12}	Liquid	Vapour	L_{12}	Liquid	Vapour
CH_4–C_3H_8	−0.07024	10.94	3.83	0.01182	2.78	3.77	0.92690	11.03	3.58	0.83670	3.18	3.71
CH_4–*n*-C_4H_{10}	−0.08256	9.06	3.79	0.03956	2.57	3.44	0.87624	9.92	3.76	0.74186	3.25	3.74
CH_4–*n*-C_5H_{12}	−0.06050	10.66	1.48	0.09939	3.09	1.32	0.78075	11.31	1.96	0.61758	3.96	2.45
CH_4–*n*-C_6H_{14}	0.19139	14.36	10.60	0.47738	3.81	10.36	0.38179	16.04	10.5	0.30011	4.51	10.52
CH_4–*n*-C_8H_{18}	−0.31336	14.85	1.34	0.22483	3.37	1.05	0.96650	15.27	2.62	0.52038	3.70	4.25
C_2H_6–*n*-C_5H_{12}	−0.07663	11.72	3.46	−0.02137	4.11	2.92	1.10919	11.04	3.47	1.03101	4.08	2.99
C_3H_8–CO_2	0.12246	14.83	2.81	0.12710	7.15	3.26	0.87683	14.42	2.67	0.87193	6.76	3.22
CH_4–H_2S	0.02131	6.64	3.75	0.09195	5.75	3.97	0.86033	6.30	2.90	0.77932	4.98	3.27
H_2S–*n*-C_5H_{12}	0.05032	18.04	6.12	0.06371	12.09	6.54	0.95397	17.47	6.20	0.93768	11.83	6.58
Average		12.34	4.13		4.97	4.07		12.53	4.18		5.14	4.53

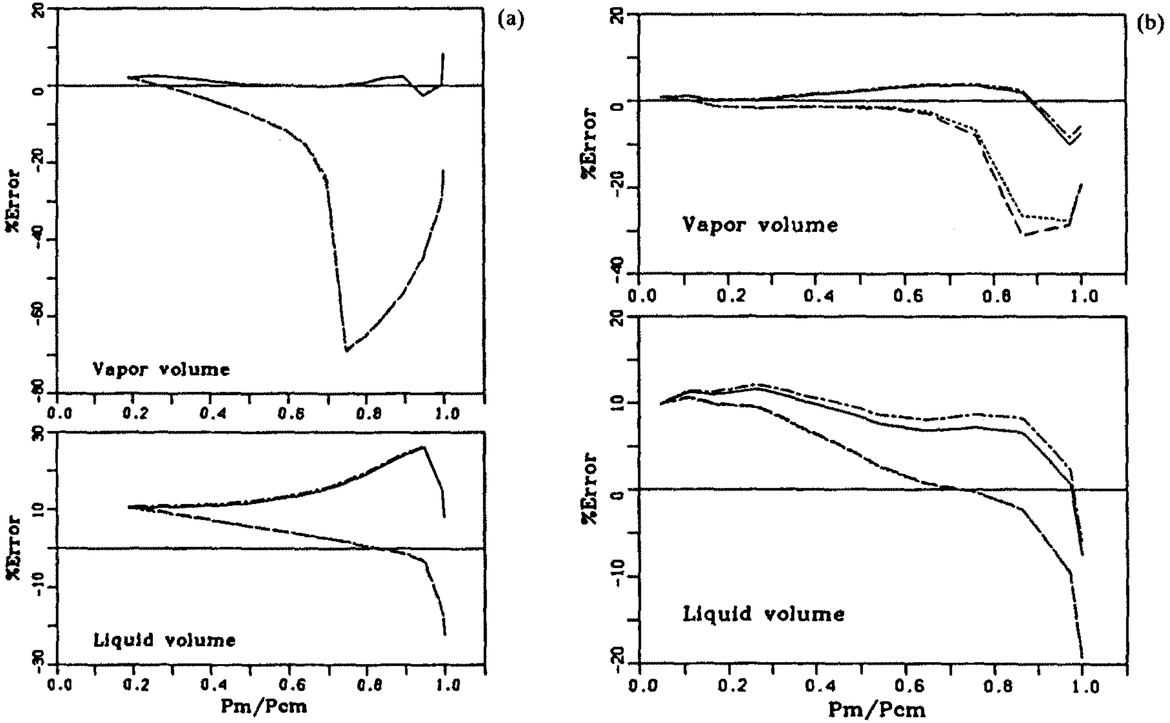

Fig. 3. % Error (eqn. (10)) of saturated liquid and vapour volume curves for (a) ethane–*n*-pentane mixture at 344.3 K; (b) propane–carbon dioxide mixture at 310.9 K. Key: —— FRKS, L_{12} taken from Table 7; · · ·, FRKS, L_{12} taken from Table 6; – · – · –, RKS, k_{12} taken from Table 7, – – –, RKS, k_{12} taken from Table 6.

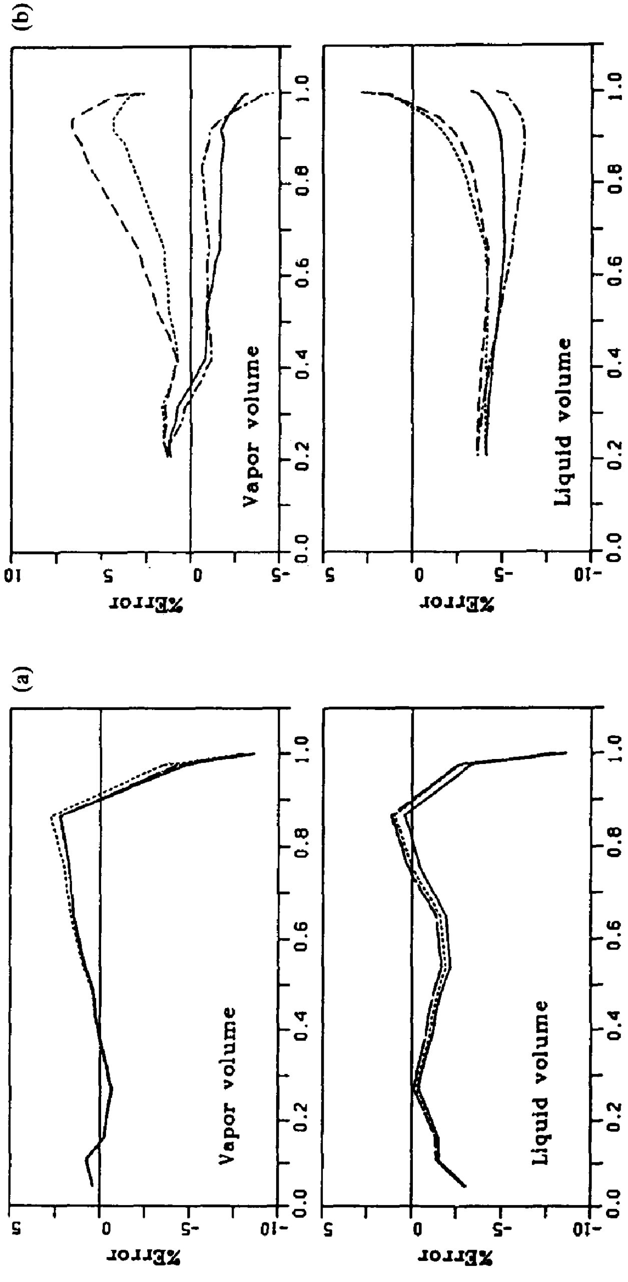

Fig. 4. % Error (eqn. (10)) of saturated liquid and vapour volume curves for (a) ethane–n-pentane mixture at 344.3 K; (b) methane–hydrogen sulphide mixture at 310.9 K. Key: ——, FPR, L_{12} taken from Table 7; · · ·, L_{12} taken from Table 6, – · – · –, PR, k_{12} taken from Table 7, – – – –, PR, k_{12} taken from Table 6.

For the FPR and PR equations, for hydrocarbon–hydrocarbon binary mixtures (Table 7, Fig. 4), the RMS% errors in liquid and vapour compressibility factors estimated by using the optimum fixed L_{ij} and k_{ij} values of Table 7 are close to those listed in Table 6. It appears that, for these binary mixtures, one can with sufficient accuracy predict saturated liquid and vapour volumes by using the optimum fixed L_{ij} or k_{ij} values obtained by minimizing the RMS% error in either the liquid or vapour state compressibility factors (Tables 6 and 7). This type of behaviour, however, is not observed for hydrocarbon–CO_2 and hydrocarbon–H_2S systems (Tables 6 and 7; Fig. 4). For these systems, the use of the L_{ij} (and k_{ij}) values (determined for vapour state) of Table 7 markedly increases the predictive accuracy of the vapour compressibility factor. In the case of such binary systems appropriate optimum L_{ij} (and k_{ij}) calculation methods should be selected.

For hydrocarbon–hydrocarbon systems, the PR equation gives somewhat better results than the FPR equation. For hydrocarbon–CO_2 and hydrocarbon–polar compound systems, the FPR equation had a slight edge over the PR equation.

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

Following the work of Lielmezs [6, 7], we introduce the following interaction parameter function $L_{ij}(T, P, x)$

$$L_{ij} = e + fx + gP + hT \tag{8}$$

into the FRKS and FPR equations. The coefficients e, f, g and h (eqn. (8)) for the FRKS and FPR equations were calculated as follows. First, the optimum L_{ij} value for every experimental data point of a given binary system was calculated by means of the Fibonacci search procedure. (The optimum L_{ij} value is that which yields the lowest RMS% error calculations for liquid and for vapour compressibility factors.) Second, upon completing the first step of calculation, the values of the coefficients e, f, g and h (eqn. (8)) were determined by means of multiproperty linear regression methods.

Table 5 presents the calculated values of coefficients e, f, g and h for the FRKS and FPR equations for the estimation of the interaction parameter L_{ij} value using eqn. (8). Table 6 compares the RMS% error values of liquid (for all 18 binary systems) and vapour (data available for only nine binary systems) compressibility factors obtained from the FRKS and FPR equations using both methods: the fixed interaction parameter L_{ij} optimum value approach (Table 4) and the binary interaction parameters function $L_{ij}(T, P, x)$ (eqn. (8)), to calculate “localized” L_{ij} values for the given T, P, x conditions (Table 5). The first four columns of Table 6 show results obtained for liquid and vapour states using the original RKS and PR equations; the next four columns (FRKS and FPR) list the results for both liquid and vapour states obtained via the fixed binary interaction parameter L_{ij} (Table 4); the last two columns (F-RKS and F-PR) present results based on the liquid state compressibility factor calculation using the interaction parameter function L_{ij} (Table 5).

Table 6 shows that, when the $L_{ij}(T, P, x)$ function (eqn. (8)) is used, the RMS% error in the liquid state compressibility factor obtained from the FRKS equation for all the systems having convergent solutions is less by 0.8–4.9 than that for the value obtained from the same equation but using fixed optimum L_{ij} values. For the FPR equation, the introduction of the $L_{ij}(T, P, x)$ function also decreases the estimated RMS% error, but not as significantly as in the case of the FRKS equation.

In concluding, we observe that the F-function modification of a cubic equation of state in general improves the performance of a two-parameter cubic equation for pure compounds and binary mixtures. Specifically, for polar and hydrogen bonded compounds, the F-function modification accurately predicts the saturated state vapour volumes and pressure. The proposed mixing rules (eqns (11–13)) coupled with the optimum fixed binary interaction parameter L_{ij} (Table 4) predict with high accuracy the compressibility factors for binary systems (Tables 6 and 7). An added improvement in the accuracy of binary mixture compressibility factor calculations has been achieved by using the binary interaction parameter function L_{ij} (eqn. (8), Table 5), as shown in Table 6.

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