Thermochimica Acta, 224 (1993) 1–12
Elsevier Science Publishers B.V., Amsterdam

Use of the binary interaction parameter $L_{ij}(T, P, x_i)$ function for van der Waals-type equations of state in vapor–liquid equilibrium calculations

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(Received 5 January 1993; accepted 2 February, 1993)

Abstract

The predictive accuracy of the newly developed binary interaction parameter function $L_{ij} = L_{ij}(T, P, x_i)$ of Lielmezs and co-workers has been studied further by means of the Redlich–Kwong–Soave (RKS) and Peng–Robinson (PR) equations of state in the vapor–liquid equilibria calculations over a wide range of P–T–x–y values. Sets of coefficients for use in the binary interaction parameter function $L_{ij} = L_{ij}(T, P, x_i)$ have been established for 29 selected binary systems.

The results calculated of the vapor–liquid equilibria (bubble point) for the binary systems considered (L-RKS, L-PR) are in excellent agreement with the experimental data and the values obtained using the F-function of two-parameter cubic equations of state (F-RKS, F-PR). The predictions made in this work (L-RKS, L-PR) have a slight edge over the results calculated via the original Redlich–Kwong–Soave (RKS) and Peng–Robinson (PR) methods.

LIST OF SYMBOLS

a, b	parameters of cubic equation of state
e, f, g, h	dimensionless coefficients of eqn. (9)
F-RKS	F-function modification of RKS equation of state with L_{ij}-function [15]
F-PR	F-function modification of PR equation of state with L_{ij}-function [15]
k_{ij}	binary interaction parameter for RKS and PR equations of state
L_{ij}	binary interaction parameter for L-RKS and L-PR equations of state
L-RKS	RKS equation with L_{ij}-function

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L-PR	PR equation with L_{ij}-function
N	number of data points
P	pressure
PR	Peng–Robinson equations of state [3]
RKS	Redlich–Kwong–Soave equation of state
R	universal gas constant
T	temperature
x	composition of liquid phase
y	composition of vapor phase

Subscripts

c	critical state
i, j	components of mixture
m	mixture

INTRODUCTION

The generalized cubic equation of state of van der Waals type can be expressed as

$$P = \frac{RT}{V-b} - \frac{a}{V^2 + ubV + wb^2} \tag{1}$$

where u and w must satisfy the constraints [1]

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

For the Redlich–Kwong–Soave (RKS) equation [2], $u = 1$ and $w = 0$; for the Peng–Robinson (PR) equation [3], $u = 2$ and $w = 1$.

Following the well-known one-fluid model of van der Waals, we write the mixing rules as

$$a_m = \sum_i \sum_j x_i x_j (a_i a_j)^{1/2} (1 - k_{ij}) \tag{3}$$

$$b_m = \sum_i x_i b_i \tag{4}$$

It has been common practice to assume that the binary interaction parameter k_{ij} (eqn. (3)) is independent of the thermodynamic state properties, i.e. temperature T, pressure P and composition x [4–8]. In recent years, some attempts have been made to correlate k_{ij} with temperature T [9–11]. Recently, following Lielmezs' work [12, 13], we successfully introduced, instead of the fixed optimum binary interaction parameter $L_{ij} = 1 - k_{ij}$, a state-dependent interaction parameter function $L_{ij}(T, P, x_i)$ into the F-function modification of the RKS and PR equations of state, F-RKS and F-PR [14–15]. In this work, we test directly the applicability of the L_{ij}-function to the original RKS and PR equations of state, denoted in this work as L-RKS and L-PR over a wide range of P–T–x–y data. To do this, experimental data of twenty-nine binary systems were selected from a number of sources. These literature data were considered of sufficient reliability so no further evaluation of their accuracy was made. The constants needed to perform the vapor–liquid equilibrium calculations, T_c, P_c and the acentric factor ω values, were taken from our previous work [14].

The calculations of the bubble-point pressure and vapor mole fractions were performed in two ways: first, via the L_{ij}-function in conjunction with the RKS and PR equations of state, identified as L-RKS and L-PR; and second, by means of the fixed averaged optimum binary interaction parameter k_{ij} ($k_{ij} = 1 - L_{ij}$), which is independent of thermodynamic state. Following our previous work [15], the optimum binary interaction parameter L_{ij} or k_{ij} values were established by means of an objective function given as

$$\mathrm{SP} = \frac{100}{N} \sum_{i}^{N} \left(\left| \frac{P_{\mathrm{cal}} - P_{\mathrm{exp}}}{P_{\mathrm{exp}}} \right|_i + |y_{\mathrm{cal}} - y_{\mathrm{exp}}|_i \right) \tag{5}$$

An optimum L_{ij} or k_{ij} value is the one that minimizes the objective function SP over the same set of experimental data.

The accuracy of the bubble point calculations is determined with reference to experimental data by means of the relative deviation of pressure ΔP (%) and the absolute deviation of vapor mole fraction Δy, defined as

$$\Delta P\,(\%) = \frac{1}{N} \sum_{i} \left| \frac{P_{\mathrm{cal}} - P_{\mathrm{exp}}}{P_{\mathrm{exp}}} \right|_i \times 100 \tag{6}$$

$$\Delta y = \frac{1}{N} \sum_{i} |y_{\mathrm{cal}} - y_{\mathrm{exp}}|_i \times 100 \tag{7}$$

All results calculated were compared to the experimental data and the values obtained by means of the original Redlich–Kwong–Soave (RKS) and Peng–Robinson (PR) equations.

BINARY INTERACTION PARAMETER FUNCTION $L_{ij}(T, P, x_i)$

It is commonly assumed that the binary interaction parameter L_{ij} (or k_{ij}) is a characteristic constant of a given binary system and, as such, is

TABLE 1

The results of bubble point calculations for the CO_2–methanol system [38] using optimum L_{12} values and the L_{12}-function

No.	T/K	P/atm	x_1	L_{12} (optimum)	ΔP/(%)	Δy_1	L_{12} (function)	ΔP/%	Δy_1
1	298.15	7.792	0.0596	0.97241	1.0158	0.218	0.97212	1.6433	0.280
2	298.15	18.814	0.1548	0.97039	0.0078	0.063	0.96835	1.5462	0.050
3	298.15	30.246	0.2601	0.96531	0.0024	0.065	0.96406	0.8698	0.070
4	298.15	39.503	0.3495	0.95671	0.0083	0.041	0.96024	2.0873	0.040
5	298.15	48.664	0.4886	0.95000	0.0010	0.035	0.95392	1.7272	0.040
6	298.15	55.013	0.6451	0.92648	0.0003	0.055	0.94620	4.5184	0.010
7	298.15	57.509	0.7685	0.86238	0.0004	0.319	0.93983	6.7092	0.000
8	298.15	58.749	0.9002	0.75789	2.2090	1.107	0.93316	4.5968	0.030
9	313.15	5.697	0.0285	0.96735	0.0084	0.260	0.95275	3.7643	0.040
10	313.15	17.469	0.1023	0.95751	0.0053	0.026	0.95028	5.3381	0.060
11	313.15	29.654	0.1641	0.94351	0.0011	0.067	0.94815	3.2101	0.090
12	313.15	40.337	0.2339	0.94256	0.0027	0.063	0.94565	2.1049	0.070
13	313.15	56.313	0.3655	0.94188	0.0064	0.153	0.94061	0.7757	0.160
14	313.15	61.903	0.4201	0.93967	0.0004	0.184	0.93835	0.7353	0.190
15	313.15	70.006	0.5429	0.93590	0.0038	0.226	0.93282	1.3053	0.270
16	313.15	76.021	0.6892	0.92412	2.8372	0.198	0.92542	3.0660	0.180
17	313.15	79.53	0.897	0.91684	5.5832	0.669	0.91464	5.5928	0.650

independent of thermodynamic state. Indeed, the fluid phase equilibria of many binary systems can be described with reasonable accuracy using fixed optimum k_{ij} or L_{ij} values, for instance, in conjunction with the RKS and PR equations of state [16]. However recent work has shown [12–15] that any small change in the k_{ij} or L_{ij} values may significantly affect prediction of the fluid phase behavior and that thermodynamic-state-dependent binary interaction parameter (k_{ij} or L_{ij}) functions may need to be introduced instead.

This need is illustrated in Table 1 and Fig. 1. Table 1 lists the fixed optimum L_{ij} values and L_{ij}-function values, calculated from the RKS equation for each individual experimental point of the CO_2–CH_3OH binary mixture. Figure 1, (a) and (b), show the fixed optimum L_{ij} values and the L_{ij}-function values, perspectively, calculated from the RKS equation plotted against pressure P and liquid-phase composition x at constant temperature T for the ethane–n-hexane and methane–n-decane binary systems. Figure 1(c) shows the fixed optimum L_{ij} and L_{ij}-function values obtained via the RKS equation plotted against temperature T and liquid-phase composition x at constant pressure P for the methane–n-decane binary system.

Table 1 and Fig. 1(a)–(c) strengthen the observation [12–15] that the binary interaction parameter L_{ij} (or k_{ij}) can be considered as a complex

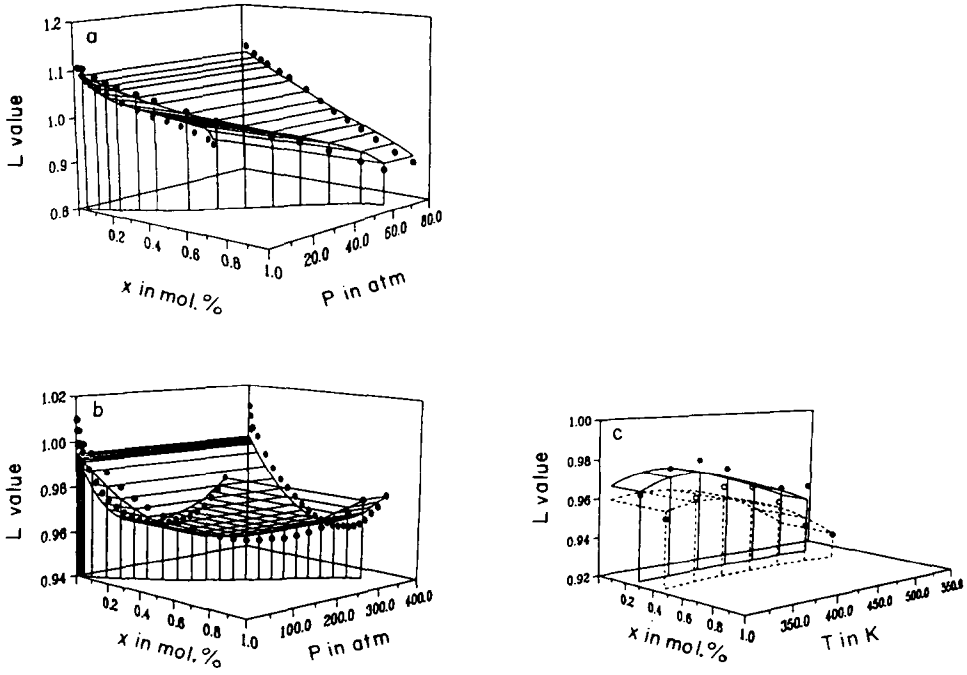

Fig. 1. (a), (b) L-value vs. mole fraction and pressure at constant temperature: ●, optimum L-value; —, L_{ij}-function for (a) the ethane–n-hexane system at $T = 338.7$ K, and (b) the methane–n-dedane system at $T = 344.26$ K. (c) L-value vs. mole fraction and temperature at constant pressure for the methane–n-decane system: ●, optimum L-value; —, L_{ij}-function, at $P = 54.5$ atm; ○, optimum L-value; · · ·, L_{ij}-function at $P = 119.0$ atm.

function of the thermodynamic state, i.e. $L_{ij} = L_{ij}(T, P, x_i)$ or $k_{ij} = k_{ij}(T, P, x_i)$.

The linear form of the L_{ij} (or k_{ij}) function can be obtained by expanding the thermodynamic-state dependency of the L_{ij}-function, $L_{ij}(T, P, x_i)$, into MacLaurin's series truncated to the first-order term, i.e.

$$L_{ij}(T, P, x_i) = L_{ij}^{o} + \frac{\partial L_{ij}}{\partial x_i} x_i + \frac{\partial L_{ij}}{\partial P} P + \frac{\partial L_{ij}}{\partial T} T \tag{8}$$

Following Lielmezs [12, 13], we identify

$$L_{ij}^{o} = e_{ij} \qquad \frac{\partial L_{ij}}{\partial x_i} = f_{ij} \qquad \frac{\partial L_{ij}}{\partial P} = g_{ij} \qquad \frac{\partial L_{ij}}{\partial T} = h_{ij} \tag{8a}$$

Putting eqn. (8a) into eqn. (8), we obtain

$$L_{ij}(T, P, x_i) = e_{ij} + f_{ij} x_i + g_{ij} P + h_{ij} T \tag{9}$$

with coefficients e_{ij}, f_{ij}, g_{ij} and h_{ij} are characteristic dimensionless constants of a given binary system [12–15].

To satisfy the requirement that $L_{ij} = 1$ and $L_{ji} = L_{ij}$, we set [15]

$$e_{ii} = 1 \qquad f_{ii} = 0 \qquad g_{ii} = 0 \qquad h_{ii} = 0$$

$$e_{ji} = e_{ij} \qquad f_{ji} = \frac{x_i}{x_j} f_{ij} \qquad g_{ji} = g_{ij} \qquad h_{ji} = h_{ij} \tag{10}$$

Putting the L_{ij}-function (eqn. (9)) into the mixing rule (eqn. (3)) for the RKS and PR equations of state, we obtain the L-RKS and L-PR equations. (For the derivation of the F-RKS and F-PR equations, see refs. 14, 15.) The values of coefficients e_{ij}, f_{ij}, g_{ij} and h_{ij} of the L-RKS and L-PR equations were determined by a method similar to that outlined in our previous work regarding the F-RKS and F-PR equations [15]. The values of the coefficients e_{ij}, f_{ij}, g_{ij} and h_{ij} (eqn. (9)) obtained for the L-RKS and L-PR equations for all 29 binary systems tested in this work are listed below in Table 3.

The vapor–liquid equilibria (bubble point) results calculated by means of the L-RKS and L-PR equations for all binary systems considered are in excellent agreement with the experimental data, and with the values obtained using the F-function of two-parameter cubic equations of state (F-RKS, F-PR [14, 15], and show a slight edge over the original RKS and PR equations (see discussion below).

RESULTS AND DISCUSSION

The introduction of the linearized L_{ij}-function (eqn. (9)) into the mixing rule (eqn. (3)) for calculating vapor–liquid equilibria has established a simple and reliable method (L-RKS, L-PR) needing nearly the same computer time as the original RKS and PR equations of state. The L_{ij}-function (eqn. (9)) was used only to provide better L_{ij} values for every point tested; it was not directly introduced into the equation of state (eqn. (1)) to derive the fugacity coefficient expression (see Appendix of ref. 15).

The bubble point calculations presented were performed following our previous work [15]. First, an initial P value was assumed; then, from this initial P, an initial L_{ij} value was obtained using (eqn. (9)), and the iteration process started. The iteration process was repeated until a preset convergence limit was reached [15].

Table 4 compares the results of the bubble point calculations performed by means of the L-RKS and L-PR equations (Table 3), the results using the original RKS and PR equations with the fixed averaged optimum k_{ij} values (Table 2) and the results obtained using the F-function of the two-parameter cubic equation, the F-RKS and F-PR equations, taken from ref. 15.

The fixed averaged optimum binary interaction parameter k_{ij} values (Table 2) were determined by minimizing the objective function SP (eqn. (5)) over all data points for a given system.

Figures 2 and 3 compare the results obtained by the methods considered

TABLE 2

Fixed optimum values of the binary interaction parameter k_{12} for use in the RKS and PR methods. [a]

System	Ref.	T range/ K	P range/ atm	Number of data points	k_{12}	
					RKS	PR
CH_4–C_2H_6	17	144–200	1–51	126	−0.02404	0.0
CH_4–C_3H_8	18	277–361	6–100	99	0.02519	0.02628
CH_4–n-C_4H_{10}	19	294–394	2–131	123	0.02418	0.02959
CH_4–n-C_6H_{14}	20	298–423	10–120	51	0.03441	0.03790
CH_4–n-C_8H_{18}	21	298–423	10–70	33	0.04571	0.04231
CH_4–n-$C_{10}H_{22}$	22	310–511	1–357	156	0.03479	0.03797
C_2H_6–C_3H_8	23	310–344	12–51	49	−0.00341	−0.00325
C_2H_6–n-C_5H_{12}	24	277–411	0–67	66	0.00553	0.00869
C_2H_6–n-C_6H_{14}	25	338–450	0–78	42	−0.02566	−0.02790
C_2H_6–n-C_8H_{18}	26	313–373	4–52	46	0.01744	0.01877
CH_4–CO_2	27	209–271	14–78	42	0.10378	0.10088
CO_2–C_2H_6	28	223–293	5–62	65	0.13682	0.12757
C_3H_8–CO_2	29	244–267	5–26	21	0.13438	0.12950
CO_2–n-C_4H_{10}	30	310–378	3–74	54	0.14267	0.13632
CO_2–n-C_5H_{12}	31	252–459	1–95	108	0.12934	0.11916
CO_2–n-C_6H_{14}	32	313–393	7–114	39	0.13937	0.12717
CO_2–n-$C_{10}H_{22}$	33	277–511	2–186	97	0.12475	0.10929
CH_4–H_2S	43	277–344	11–133	62	0.08266	0.08273
C_2H_6–H_2S	34	200–283	1–30	43	0.08573	0.08264
H_2S–C_3H_8	35	217–344	1–27	41	0.08502	0.08207
H_2S–n-C_5H_{12}	36	277–411	0–89	55	0.08407	0.07214
H_2S–n-$C_{10}H_{22}$	37	277–444	1–132	55	0.04529	−0.10002
CO_2–methanol	38	298–313	5–80	17	0.02356	0.05277
Acetone–CO_2	39	298–313	4–73	25	0.00644	0.01073
Acetone–methanol	40	373–473	3–39	39	−0.00491	−0.00378
Acetone–H_2O	40	373–523	3–67	69	−0.12428	−0.12335
Methanol–H_2O	40	373–523	1–84	56	−0.08116	−0.08131
Ethanol–H_2O	41	423–623	5–187	85	−0.08528	−0.08344
NH_3–H_2O	42	333–420	0–16	63	−0.28314	−0.26532

[a] Apart from the CH_4–n-$C_{10}H_{12}$, CO_2–n-C_5H_{22}, CO_2–n-$C_{10}H_{22}$, C_2H_6–H_2S, and H_2S–n-$C_{10}H_{22}$ systems, all the k_{12} values were taken from our previous work [15].

in this work. Both Table 4 and Figs. 2 and 3 show that the L-RKS and L-PR equations predict with high accuracy the vapor–liquid equilibrium for all systems tested. Table 4 shows that for hydrocarbon–hydrocarbon, CO_2–hydrocarbon and H_2S-hydrocarbon binary systems, the predictive accuracy hardly differs between the F-RKS and L-RKS, and F-PR and L-PR calculation methods. However, the polar–polar mixtures such as CH_3OH–H_2O, C_2H_5OH–H_2O and NH_3–H_2O, the F-RKS and F-PR methods predict more accurately than the L-RKS and L-PR methods.

TABLE 3

Coefficients of the function $L_{11} = e_{12} + f_{12}x_1 + g_{12}P + h_{12}T$ (eqn. (9)) for use in the L-RKS and L-PR methods

System	L-RKS				L-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	0.95678	0.20630	−0.03228	0.25792	0.97502	0.02820	−0.01453	0.14203
CH_4–C_3H_8	0.96575	2.69301	−0.18347	0.10858	0.77294	4.80360	−0.31277	0.78981
CH_4–n-C_4H_{10}	0.99214	2.84307	−0.13978	−0.03766	0.90420	3.68099	−0.17669	0.22783
CH_4–n-C_6H_{14}	1.27305	−5.70018	0.21552	−0.92034	1.17254	−3.73739	0.14366	−0.63260
CH_4–n-C_8H_{18}	1.11264	−5.35230	0.22497	−0.49815	1.04113	−3.53205	0.15731	−0.29230
CH_4–n-$C_{10}H_{22}$	1.04558	−1.67465	0.03516	−0.16053	1.04812	−2.64264	0.05582	−0.15242
C_2H_6–n-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}	1.02175	0.03561	−0.03726	−0.06636	1.02775	−0.05579	−0.03207	−0.08875
C_2H_6–n-C_6H_{14}	1.63388	−3.28189	0.08754	−1.52848	1.38630	−2.96431	0.04223	−0.79208
C_2H_6–C_8H_{18}	0.98776	0.16048	−0.03105	−0.01241	0.98791	0.03148	−0.01343	−0.01453
CH_4–CO_2	1.13181	−0.88547	0.03905	−0.97922	0.97457	0.07887	0.00875	−0.35275
CO_2–C_2H_6	0.71901	0.14449	−0.09018	0.62547	0.85087	0.10031	0.02102	0.02498
C_3H_8–CO_2	0.85142	−0.31832	−0.08408	0.17137	0.85780	−0.24547	−0.06211	0.13545
CO_2–n-C_4H_{10}	0.86740	0.66946	−0.06727	−0.02491	0.88476	0.31487	−0.01971	−0.06519
CO_2–n-C_5H_{12}	0.82959	0.48544	−0.04625	0.13727	0.82262	0.41132	−0.04028	0.19084
CO_2–n-C_6H_{14}	0.89448	0.53183	−0.01009	−0.13630	0.84932	0.89857	−0.03312	0.02710
CO_2–n-$C_{10}H_{22}$	0.85965	0.18911	0.00758	0.00226	0.85092	0.42523	−0.00591	0.06351
CH_4–H_2S	0.91136	2.77753	−0.07310	0.05526	0.91136	2.77753	−0.07310	0.05526
C_2H_6–H_2S	0.90915	−0.08189	0.00688	0.02888	0.94067	−0.14024	0.03764	−0.09888
H_2S–C_3H_8	0.85137	0.34481	−0.01858	0.18752	0.91210	0.41049	0.02319	−0.04321
H_2S–n-C_5H_{12}	0.89305	0.56079	−0.09912	0.12477	0.91044	0.26112	−0.04373	0.10172
H_2S–n-$C_{10}H_{22}$	0.87430	0.76052	−0.10508	0.20697	0.86116	0.75622	−0.12541	0.29363
CO_2–methanol	1.38707	−0.52619	0.01090	−1.38403	1.40858	−1.52278	0.08727	−1.46565
Acetone–CO_2	1.13300	0.53069	0.07482	−0.62326	1.15952	1.10006	0.15253	−0.89983
Acetone–methanol	1.07747	−0.61707	−0.05404	−0.08670	1.19273	−0.47673	0.06230	−0.42300
Acetone–H_2O	1.16179	−0.94069	−0.13223	0.05279	1.19165	−0.82978	−0.09977	−0.04018
Methanol–H_2O	1.07973	0.26495	−0.01904	−0.00674	1.10790	0.29725	−0.01768	−0.07261
Ethanol–H_2O	1.11565	−0.27200	−0.00615	−0.04271	1.09793	−0.29670	−0.03666	0.00776
NH_3–H_2O	1.24890	1.64573	−0.20002	0.04408	1.35090	1.17887	−0.10407	−0.26864

TABLE 4

Comparison of bubble-point calculations by different methods

System	RKS			F-RKS			L-RKS			PR			F-PR			L-PR		
	$\Delta P/\%$	Δy_1	Rej.[a]	$\Delta P/\%$	Δy_1	Rej.[a]	$\Delta P/\%$	Δy_1	Rej.[a]	$\Delta P/\%$	Δy_1	Rej.[a]	$\Delta P/\%$	Δy_1	Rej.[a]	$\Delta P/\%$	Δy_1	Rej.[a]
CH_4–C_2H_6	2.04	0.62	6	2.01	0.39	5	1.39	0.42	6	2.05	0.76	7	1.88	0.29	6	1.36	0.39	7
CH_4–C_3H_8	1.68	1.23	8	1.44	0.99	5	1.15	1.12	7	1.52	1.38	9	1.83	1.32	8	1.16	1.38	8
CH_4–n-C_4H_{10}	2.62	1.86	0	2.05	1.63	0	1.86	1.83	0	2.55	1.53	0	2.00	1.21	0	2.13	1.38	0
CH_4–n-C_6H_{14}	2.62	1.45	0	1.85	1.57	0	1.69	1.45	0	2.09	1.38	0	1.70	1.41	0	1.49	1.32	0
CH_4–n-C_8H_{18}	2.47	0.31	0	1.04	0.20	0	0.90	0.22	0	1.95	0.38	0	1.23	0.29	0	0.89	0.34	0
CH_4–n-$C_{10}H_{22}$	2.43	0.59	2	–	–	–	2.35	0.63	2	2.98	0.34	0	–	–	–	1.78	0.37	0
C_2H_6–C_3H_8	2.20	1.18	11	1.33	0.78	8	1.60	1.11	11	2.19	1.53	10	2.34	1.52	10	1.91	1.25	10
C_2H_6–n-C_5H_{12}	2.01	1.13	0	1.90	0.78	0	2.70	0.87	0	2.29	0.93	0	2.15	0.85	0	2.02	0.90	0
C_2H_6–n-C_6H_{14}	11.23	2.26	0	3.96	2.08	0	4.82	2.04	0	11.13	2.37	0	4.44	2.40	0	4.19	2.53	0
C_2H_6–n-C_8H_{18}	1.56	0.78	0	1.37	0.77	0	1.44	0.78	0	1.54	0.74	0	1.47	0.75	0	1.48	0.74	0
Average	3.19	1.14		1.88	1.02		1.93	1.05		3.03	1.13		2.12	1.12		1.84	1.06	
CH_4–CO_2	2.60	1.06	0	2.56	1.20	0	2.42	1.07	0	2.56	1.08	0	2.99	1.38	0	2.42	0.90	0
CO_2–C_2H_6	0.67	0.51	4	0.59	0.38	2	0.65	0.49	0	1.23	0.56	3	0.70	0.38	3	0.41	0.50	4
C_3H_8–CO_2	1.75	0.52	0	1.41	0.53	0	1.44	0.50	0	1.57	0.50	0	1.46	0.52	0	1.41	0.46	0
CO_2–n-C_4H_{10}	2.00	1.03	0	0.99	0.78	0	0.84	0.70	0	1.82	0.97	0	1.37	0.85	0	1.26	0.79	0
CO_2–n-C_5H_{12}	2.45	1.16	8	–	–	–	2.15	1.19	8	2.41	1.30	9	–	–	–	2.14	1.35	9
CO_2–n-C_6H_{14}	2.21	0.64	0	1.26	0.61	0	0.99	0.60	0	1.99	0.70	0	1.23	0.56	0	1.27	0.60	0
CO_2–n-$C_{10}H_{22}$	3.52	0.92	0	–	–	–	2.58	0.85	0	3.60	0.92	0	–	–	–	2.76	0.90	0
CH_4–H_2S	3.29	2.06	3	–	–	–	2.36	1.86	2	3.67	2.17	4	–	–	–	2.80	1.89	3
C_2H_6–H_2S	1.27	1.89	0	–	–	–	1.01	1.98	0	1.27	2.18	0	–	–	–	0.88	2.30	0
H_2S–C_3H_8	2.78	1.75	0	1.96	1.94	0	1.69	1.86	0	2.69	1.71	0	1.92	1.53	0	1.57	1.69	0
H_2S–n-C_5H_{12}	5.01	1.87	1	2.05	1.68	1	2.67	1.52	0	4.31	1.89	1	2.49	2.02	0	3.26	1.62	0
H_2S–n-$C_{10}H_{22}$	4.68	0.27	0	–	–	–	2.66	0.32	0	4.86	0.36	0	–	–	–	2.17	0.54	0
Average	2.69	1.14		1.55	1.02		1.79	1.08		2.67	1.20		1.74	1.03		1.86	1.13	
CO_2–methanol	12.10	0.27	0	3.01	0.20	0	2.92	0.13	0	6.99	0.20	0	4.06	0.22	0	3.44	0.20	0
Acetone–CO_2	0.98	0.27	0	0.84	0.17	0	0.72	0.26	0	1.02	0.19	0	0.86	0.14	0	0.88	0.18	0
Acetone–methanol	2.02	2.14	0	1.82	2.66	0	1.39	2.19	0	2.17	2.05	0	1.79	2.67	0	1.14	2.11	0
Acetone–H_2O	5.08	3.14	0	3.38	2.44	0	2.40	2.72	0	5.12	3.28	0	3.40	2.48	0	2.49	2.95	0
Methanol–H_2O	2.22	1.80	0	0.95	1.01	0	1.86	2.11	0	2.35	1.53	0	0.98	0.95	0	1.67	1.76	0
Ethanol–H_2O	2.12	1.42	3	1.14	1.20	3	1.60	1.29	3	2.08	1.41	4	1.24	1.23	4	1.57	1.24	3
NH_3–H_2O	8.52	2.51	0	1.82	1.85	0	3.88	4.39	0	6.95	2.05	0	4.21	2.33	0	4.09	2.58	0
Average	4.71	1.65		1.85	1.36		2.11	1.87		3.81	1.53		2.36	1.43		2.18	1.57	

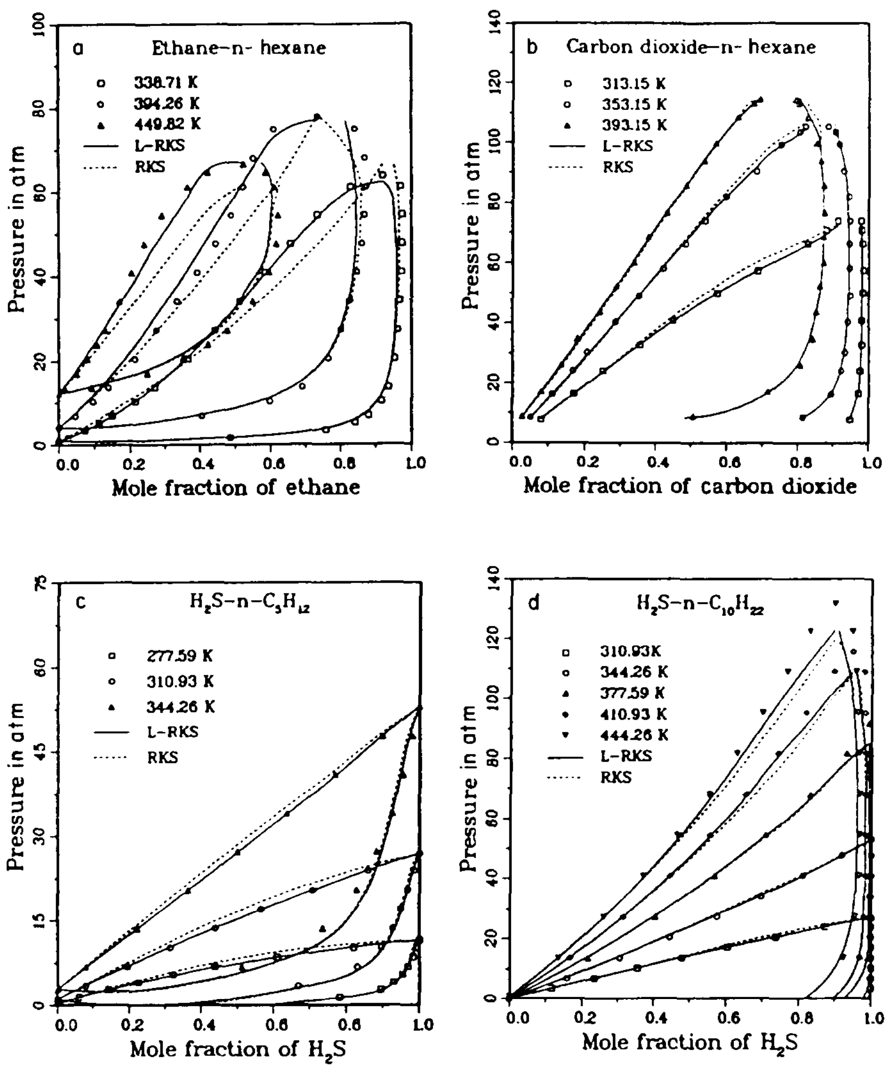

Fig. 2. Comparison of the calculated (L-RKS and RKS) and experimental vapor–liquid equilibria values for (a) ethane–*n*-hexane [25]; (b) carbon dioxide–*n*-hexane [32]; (c) hydrogen sulphide–*n*-pentane [36]; (d) hydrogen sulphide–*n*-decane [37].

ACKNOWLEDGEMENTS

The financial assistance of the Natural Science and Engineering Research Council of Canada is gratefully acknowledged. Mrs. H. Aleman is thanked for her contribution regarding the preparation of this manuscript.

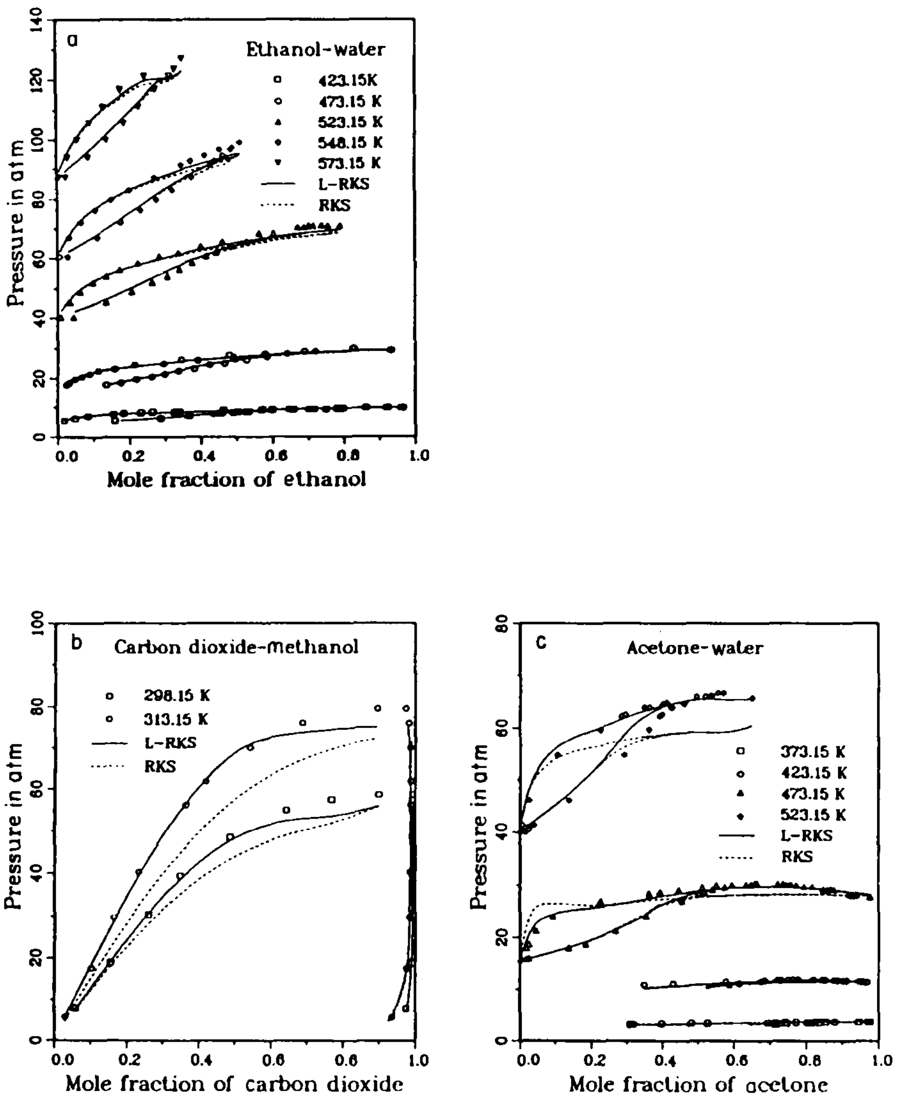

Fig. 3. Comparison of calculated (L-RKS and RKS) and experimental vapor–liquid equilibria values for (a) ethanol–water [41]; (b) carbon dioxide–methanol [38]; (c) acetone–water [40].

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