Thermochimica Acta, 231 (1994) 297–306
Elsevier Science B.V., Amsterdam
SSDI 0041-6031(93)01353-5

Application of LM modification of a cubic equation of state for vapor–liquid equilibrium calculations of binary mixtures

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(Received 31 March 1993; accepted 10 May 1993)

Abstract

The Lielmezs–Merriman (LM) modification of the Peng–Robinson (PR) equation of state has been expanded to vapor–liquid equilibrium predictions of binary mixtures. The predicted bubble point pressures and vapor mole fractions have been compared with the results calculated by the Redlich–Kwong–Soave (RKS), Peng–Robinson (PR) equations and F-function modifications of RKS (FRKS, F-RKS) and PR (FPR, F-PR) equations.

NOMENCLATURE

a, b	parameters of cubic equation of state
e, f, g, h	dimensionless coefficients of eqn. (13)
FRKS	F-function modification of RKS equation of state [6]
F-RKS	FRKS equation with L_{ij}-function [6]
FPR	F-function modification of PR equation of state
F-PR	FPR equation with L_{ij}-function [6]
k_{ij}	binary interaction parameter for RKS and PR equations of state
L_{ij}	binary interaction parameter [5, 6]
LM	Lielmezs and Merriman modification of the PR equation of state [1]
L-LM	LM equation with L_{ij}-function
L-RKS	RKS equation with L_{ij}-function [5]
L-PR	PR equation with L_{ij}-function [5]
N	number of data points
p	substance-dependent parameter in eqn. (5)
P	pressure

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PR	Peng–Robinson equation of state [2]
q	substance-dependent parameter in eqn. (5)
R	universal gas constant
RKS	Redlich–Kwong–Soave equation of state [7]
T	temperature
x	composition of liquid phase
y	composition of vapor phase

Subscripts

c	critical state
i, j	components of mixture
m	mixture

INTRODUCTION

Earlier, Lielmezs and Merriman [1] proposed a modification of the Peng–Robinson [2] equation of state for predicting the saturated states of vapor–liquid equilibrium. Recently, Lielmezs and Mak [3, 4] extended this modification for pure substances to include the entire (except the critical isotherm) P–V–T surface. The LM modification of Peng–Robinson equation of state can be expressed as [1, 3]

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

where

$$b = 0.07780\frac{RT_c}{P_c} \tag{2}$$

$$a(T) = a(T_c, P_c)\alpha(T^*) \tag{3}$$

In eqn. (3), the first term is written as

$$a(T_c, P_c) = 0.45724\frac{R^2T_c^2}{P_c} \tag{4}$$

and the second term $\alpha(T^*)$ is modified as

$$\alpha(T^*) = 1 \pm p(T^*)^q \tag{5}$$

where the p and q are characteristic constants of a given pure compound and can be determined by curve-fitting to experimental data of the given pure compound.

The (+) and (−) signs in eqn. (5) are applied to the temperature regions of $T < T_c$ and $T > T_c$, respectively. The dimensionless temperature T^* (eqn. (5)) is defined as

$$T^* = \frac{\left(\frac{T_c}{T}\right) - 1}{\left(\frac{T_c}{T_b}\right) - 1} \quad \text{for } T < T_c \tag{6}$$

$$T^* = \frac{\left(\frac{T}{T_c}\right) - 1}{\left(\frac{T_c}{T_b}\right) - 1} \quad \text{for } T > T_c \tag{7}$$

In the case of a binary mixture where one or even both components may be found in the supercritical state, Lielmezs and Mak's modification (eqns. (5)–(7)) permits use of the LM equation directly for vapor–liquid equilibrium calculations.

To test the applicability of the LM equation to vapor–liquid equilibrium calculations of binary mixtures, the experimental data of the twenty three binary systems for which the p and q constant values are available (Lielmezs and Mak [3]) were taken from the sources listed in ref. 5. The testing was done in two ways: first, by means of fixed averaged optimum binary interaction parameter L_{ij} values independent of thermodynamic states (LM, Table 1), and secondly, via the binary interaction parameter L_{ij}-function, $L_{ij}(T, P, x_i)$ (L-LM, Table 2). The constants needed for vapor–liquid equilibrium calculations, the T_c, T_B, P_c and acentric factor ω values were taken from the work of Lielmezs and Mak [3]. The one fluid mixing rules of van der Waals were used for LM equation

$$a_m = \sum_i \sum_j x_i x_j (a_i a_j)^{1/2} L_{ij} \tag{8}$$

$$b_m = \sum_i x_i b_i \tag{9}$$

where $L_{ij} = 1 - k_{ij}$.

The objective function used for determining the optimum binary parameter L_{ij} values is given as [6]

$$SP = \frac{100}{N} \sum_i^N \left(\left| \frac{P_{cal} - P_{exp}}{P_{exp}} \right|_i + |y_{cal} - y_{exp}|_i \right) \tag{10}$$

The accuracy of bubble point calculations is evaluated by means of

TABLE 1

Comparison of bubble point calculations by LM, RKS, FRKS, PR and FPR methods using fixed optimum values of binary parameter L_{12} (or k_{12})[a]

System	LM			RKS			FRKS			PR			FPR		
	$\Delta P/\%$	Δy_1	Rej.[b]	$\Delta P/\%$	Δy_1	Rej.[b]	$\Delta P/\%$	Δy_1	Rej.[b]	$\Delta P/\%$	Δy_1	Rej.[b]	$\Delta P/\%$	Δy_1	Rej.[b]
CH_4–C_2H_6	1.65	0.54	8	2.04	0.62	6	2.65	0.52	5	2.05	0.76	7	2.05	0.25	7
CH_4–C_3H_8	1.90	1.37	8	1.68	1.23	8	4.88	1.21	7	1.52	1.38	9	4.68	1.72	8
CH_4–n-C_4H_{10}	3.02	1.57	0	2.62	1.86	0	6.46	1.98	0	2.55	1.53	0	7.39	1.84	0
CH_4–n-C_6H_{14}	3.19	1.78	0	2.62	1.45	0	10.71	1.75	0	2.09	1.38	0	12.25	1.90	0
CH_4–n-C_8H_{18}	3.41	0.38	0	2.47	0.31	0	11.79	0.62	0	1.95	0.38	0	14.28	0.81	0
C_2H_6–n-C_3H_8	1.93	0.81	11	2.20	1.18	11	1.83	1.02	9	2.19	1.53	10	2.05	0.78	10
C_2H_6–n-C_5H_{12}	2.48	0.82	0	2.01	1.13	0	1.86	0.81	0	2.29	0.93	0	2.21	0.88	0
C_2H_6–n-C_6H_{14}	11.80	2.18	0	11.23	2.26	0	9.76	2.22	0	11.31	2.37	0	10.59	2.18	0
C_2H_6–n-C_8H_{19}	1.96	0.73	0	1.56	0.78	0	1.40	0.77	0	1.54	0.74	0	1.45	0.75	0
Average	3.13	1.02		3.16	1.20		5.71	1.21		3.03	1.22		6.33	1.23	
CH_4–CO_2	2.63	1.40	0	2.60	1.06	0	5.49	1.50	0	2.56	1.08	0	4.18	1.71	0
CO_2–C_2H_6	0.71	0.44	4	0.67	0.51	4	0.76	0.47	2	1.23	0.56	3	0.81	0.46	3
C_3H_8–CO_2	1.96	0.53	0	1.75	0.52	0	2.01	0.52	0	1.57	0.50	0	2.03	0.52	0
CO_2–n-C_4H_{10}	1.44	1.00	0	2.00	1.03	0	1.48	0.84	0	1.82	0.97	0	1.58	0.90	0
CO_2–n-C_5H_{12}	2.32	1.43	7	2.45	1.16	8				2.41	1.30	9			
CO_2–n-C_6H_{14}	2.10	0.75	0	2.21	0.64	0	3.13	0.70	0	1.99	0.70	0	2.36	0.71	0
CH_4–H_2S	3.71	2.02	2	3.29	2.06	3				3.67	2.17	4			
C_2H_6–H_2S	1.55	1.18	0	1.27	1.89	0				1.27	2.18	0			
H_2S–C_3H_8	2.37	1.90	0	2.78	1.75	0	3.41	1.97	0	2.69	1.71	0	3.32	1.97	0
H_2S–n-C_5H_{12}	3.85	1.57	1	5.01	1.87	1	3.26	1.41	1	4.31	1.89	1	3.22	1.61	1
Average	2.26	1.22		2.40	1.25		2.79	1.07		2.35	1.31		2.50	1.13	
CO_2–CH_3OH	6.69	0.19	0	12.01	0.27	0	6.37	0.17	0	6.99	0.20	0	6.73	0.19	0
CH_3OH–H_2O	4.01	1.00	0	2.22	1.80	0	1.59	1.05	0	2.35	1.53	0	1.81	1.05	0
C_2H_5OH–H_2O	2.76	1.46	1	2.12	1.42	3	2.30	1.30	3	2.08	1.41	4	2.36	1.38	4
NH_3–H_2O	4.41	2.56	0	8.52	2.51	0	3.97	2.06	0	6.95	2.05	0	5.00	1.91	0
Average	4.52	1.30		6.22	1.50		3.56	1.15		4.59	1.30		3.98	1.13	

[a] References taken from our previous work [5, 6]. [b] Number of rejected data points.

TABLE 2

Comparison of bubble point calculations by L-LM, L-RKS, F-RKS, L-PR and F-PR methods using L_{12}-function (eqn. (13))[a]

System	L-LM			L-RKS			F-RKS			L-PR			F-PR		
	$\Delta P/\%$	Δy_1	Rej.[b]	$\Delta P/\%$	Δy_1	Rej.[b]	$\Delta P/\%$	Δy_1	Rej.[b]	$\Delta P/\%$	Δy_1	Rej.[b]	$\Delta P/\%$	Δy_1	Rej.[b]
CH_4–C_2H_6	1.28	0.35	8	1.39	0.42	6	2.01	0.39	5	1.36	0.39	7	1.88	0.29	6
CH_4–C_3H_8	1.24	1.27	8	1.15	1.12	7	1.44	0.99	5	1.16	1.38	8	1.83	1.32	8
CH_4–n-C_4H_{10}	1.89	1.47	0	1.86	1.83	0	2.05	1.63	0	2.13	1.38	0	2.00	1.21	0
CH_4–n-C_6H_{14}	1.26	1.33	0	1.69	1.45	0	1.85	1.57	0	1.49	1.32	0	1.70	1.41	0
CH_4–n-C_8H_{18}	0.95	0.35	0	0.90	0.22	0	1.04	0.20	0	0.89	0.34	0	1.23	0.29	0
C_2H_6–n-C_3H_8	2.16	1.33	10	1.60	1.11	11	1.33	0.78	8	1.91	1.25	10	2.34	1.52	10
C_2H_6–n-C_5H_{12}	2.35	0.92	0	2.07	0.87	0	1.90	0.78	0	2.02	0.90	0	2.15	0.85	0
C_2H_6–n-C_6H_{14}	4.29	2.28	0	4.82	2.04	0	3.96	2.08	0	4.19	2.53	0	4.44	2.40	0
C_2H_6–n-C_8H_{18}	1.38	0.74	0	1.44	0.78	0	1.37	0.77	0	1.48	0.74	0	1.47	0.75	0
Average	1.87	1.12		1.88	1.09		1.88	1.02		1.85	1.14		2.12	1.12	
CH_4–CO_2	2.26	1.29	0	2.42	1.07	0	2.56	1.20	0	2.42	0.90	0	2.99	1.38	0
CO_2–C_2H_6	0.56	0.34	4	0.65	0.49	0	0.59	0.38	2	0.41	0.50	4	0.70	0.38	3
C_3H_8–CO_2	1.47	0.53	0	1.44	0.50	0	1.41	0.53	0	1.41	0.46	0	1.46	0.52	0
CO_2–n-C_4H_{10}	0.76	0.83	0	0.84	0.70	0	0.99	0.78	0	1.26	0.79	0	1.37	0.85	0
CO_2–n-C_5H_{12}	2.02	1.38	8	2.15	1.19	8				2.14	1.35	9			
CO_2–n-C_6H_{14}	1.33	0.68	0	0.99	0.60	0	1.26	0.61	0	1.27	0.60	0	1.23	0.56	0
CH_4–H_2S	2.67	1.88	2	2.36	1.86	2				2.80	1.89	3			
C_2H_6–H_2S	0.91	1.18	0	1.01	1.98	0				0.88	2.30	0			
H_2S–C_3H_8	1.60	1.91	0	1.69	1.86	0	1.96	1.94	0	1.57	1.69	0	1.92	1.53	0
H_2S–n-C_5H_{12}	2.32	1.93	0	2.67	1.52	0	2.05	1.68	1	3.26	1.62	0	2.49	2.02	0
Average	1.59	1.20		1.62	1.18		1.55	1.02		1.74	1.21		1.74	1.03	
CO_2–CH_3OH	2.39	0.21	0	2.92	0.13	0	3.01	0.20	0	3.44	0.20	0	4.06	0.22	0
CH_3OH–H_2O	2.57	1.68	0	1.86	2.11	0	0.95	1.01	0	1.67	1.76	0	0.98	0.95	0
C_2H_5OH–H_2O	1.74	1.79	3	1.60	1.29	3	1.14	1.20	3	1.57	1.24	3	1.24	1.23	4
NH_3–H_2O	2.55	2.16	0	3.88	4.39	0	1.82	1.85	0	4.09	2.58	0	4.21	2.33	0
Average	2.31	1.46		2.57	1.98		1.73	1.07		2.69	1.45		2.62	1.18	

[a] References taken from our previous work [5, 6]. [b] Number of rejected data points.

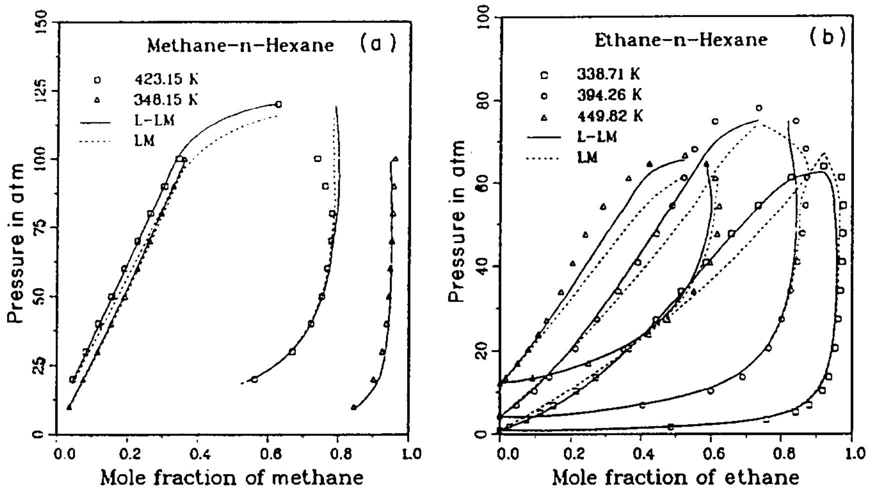

Fig. 1. Comparison of calculated (L-LM and LM) and experimental vapor–liquid equilibria values for (a) methane–*n*-hexane [10], (b) ethane–*n*-hexane [11].

relative deviation of pressure $\Delta P(\%)$ and absolute deviation of vapor mole fraction Δy, defined as [6]

$$\Delta P(\%) = \frac{1}{N}\sum_i \left|\frac{P_{\text{cal}} - P_{\text{exp}}}{P_{\text{exp}}}\right|_i \times 100 \tag{11}$$

$$\Delta y = \frac{1}{N}\sum_i |y_{\text{cal}} - y_{\text{exp}}|_i \times 100 \tag{12}$$

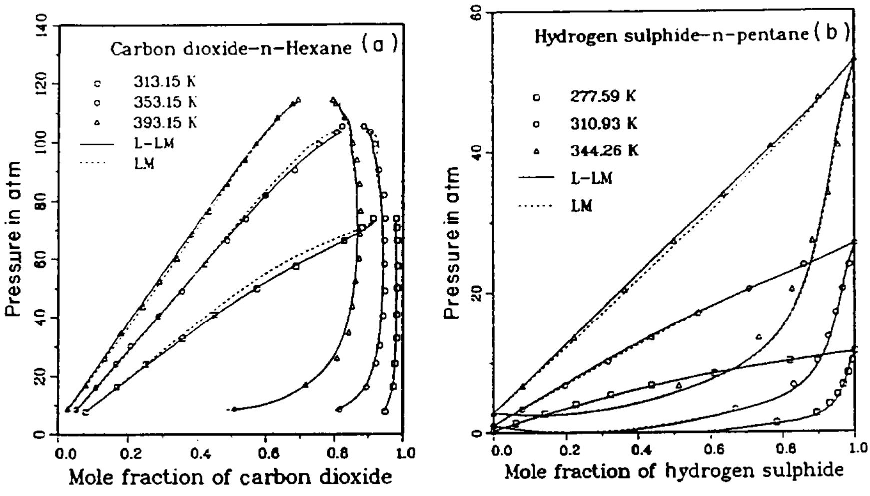

Fig. 2. Comparison of calculated (L-LM and LM) and experimental liquid–vapor equilibria values for (a) carbon dioxide–*n*-hexane [12], (b) hydrogen sulphide–*n*-pentane [13].

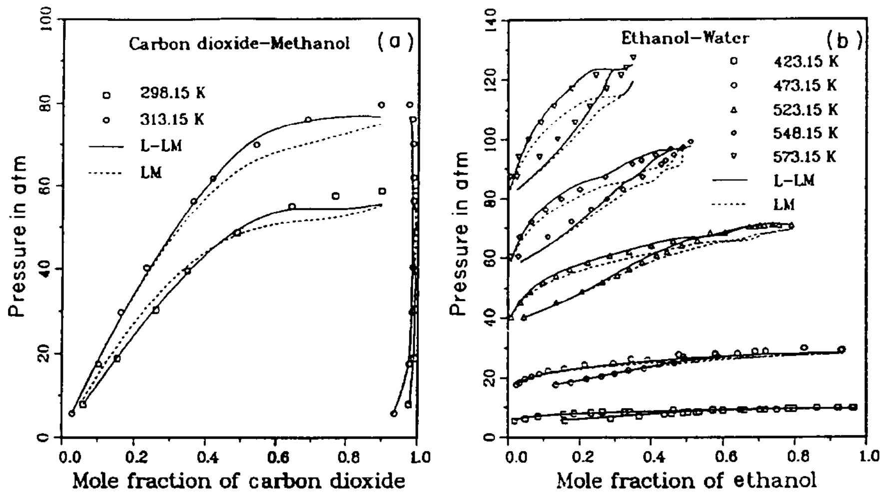

Fig. 3. Comparison of calculated (L-LM and LM) and experimental vapor–liquid equilibria values for (a) carbon dioxide–methanol [14], (b) ethanol–water [15].

All the results calculated from LM equation with both fixed optimum L_{ij} values and L_{ij}-function were compared to the experimental data available and the results obtained by means of the original RKS [7] and PR [2] equations, and F-function modifications of RKS and PR equations, denoted as FRKS, F-RKS and FPR, F-PR [5, 6] (Tables 1 and 2, Figs. 1–3).

RESULTS AND DISCUSSION

Fixed optimum L_{ij} *values*

Following methods of our previous work [6], the fixed averaged optimum binary interaction parameter L_{ij} values of all the twenty-three systems tested for use in the LM equation were determined by minimizing the objective function SP (eqn. (10)) over the same set of experimental data of a given system. The resulting L_{ij} values are presented in Table 3.

Table 1 compares the results of bubble point calculations obtained by means of fixed optimum L_{ij} (or K_{ij}) values using the following methods: LM equation (this work), original RKS and PR equations [5], and F-function modifications (FRKS and FPR) of RKS and PR equations [6].

From Table 1, it is seen that if fixed optimum L_{ij} values are used, the LM equation predicts the vapor–liquid equilibria of binary systems with reasonable accuracy. For hydrocarbon–hydrocarbon systems, LM, RKS, and PR equations are similar in accuracy, while FRKS and FPR equations show higher average $\Delta P(\%)$ and Δy_1 values. For CO_2–hydrocarbon and

TABLE 3

Fixed average optimum L_{ij} values for use in LM method and coefficients of function $L_{12} = e_{12} + f_{12}x_1 + g_{12}P + h_{12}T$ (eqn. (13)) for use in the L-LM method[a]

System	LM	L-LM			
	L_{12}	e_{12}	$f_{12} \times 10$	$g_{12} \times 10^2$	$h_{12} \times 10^3$
CH_4–C_2H_6	1.0	0.97501	0.02820	−0.01453	0.14203
CH_4–C_3H_8	0.96260	0.98232	2.58539	−0.17361	−0.00853
CH_4–*n*-C_4H_{10}	0.95509	1.05664	3.04110	−0.15198	−0.30396
CH_4–*n*-C_6H_{14}	0.94601	1.16489	−2.45907	0.09591	−0.66625
CH_4–*n*-C_8H_{18}	0.93765	1.06793	−2.29793	0.11487	−0.43755
C_2H_6–C_3H_8	1.01033	1.68135	−1.14226	0.21111	−2.18346
C_2H_6–*n*-C_5H_{12}	0.99077	1.01974	0.17100	−0.04451	−0.07698
C_2H_6–*n*-C_6H_{14}	1.02004	1.51732	−3.38674	−0.10096	−1.16151
C_2H_6–*n*-C_8H_{18}	0.98310	1.01917	0.21538	−0.03275	−0.11264
CH_4–CO_2	0.89645	1.00604	−0.08486	−0.01161	−0.43320
CO_2–C_2H_6	0.87281	0.79084	0.17803	−0.06185	0.34460
C_3H_8–CO_2	0.87464	0.84026	−0.55330	−0.18295	0.35696
CO_2–*n*-C_4H_{10}	0.86458	0.85398	1.04880	−0.09863	0.04860
CO_2–*n*-C_5H_{12}	0.87876	0.86589	0.37078	−0.02941	0.03319
CO_2–*n*-C_6H_{14}	0.86811	0.96480	0.26221	0.00875	−0.31465
CH_4–H_2S	0.90916	0.94738	0.76758	−0.00050	−0.18236
C_2H_6–H_2S	0.91623	0.91710	−0.16640	−0.02840	0.01145
H_2S–C_3H_8	0.91439	0.76979	0.51770	−0.21655	0.52567
H_2S–*n*-C_3H_{12}	0.94721	0.94638	0.29476	−0.06059	−0.03177
CO_2–CH_3OH	0.93771	1.44203	−1.44623	0.08853	−1.61796
CH_3OH–H_2O	0.08148	1.41971	−0.68658	0.14612	−0.79956
C_2H_5OH–H_2O	1.08213	1.09793	−0.29670	−0.03666	0.00776
NH_3–H_2O	1.26724	1.29040	0.60756	−0.16498	−0.07681

[a] References taken from our previous work [5,6].

H_2S–hydrocarbon systems, all five methods of calculation predict with the same accuracy. For polar–polar systems, the FRKS and FPR equation show a slight edge over the LM, RKS and PR methods.

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

Following Lielmezs [8, 9], recently, we successfully introduce, instead of the fixed optimum binary interaction prameter L_{ij}, where $L_{ij} = 1 - k_{ij}$, a state dependent interaction parameter function $L_{ij}(T, P, x_i)$ into the F-function modifications of RKS and PR equations [6], and the original RKS and PR equations. In this work, however, we test the applicability of the interaction parameter L_{ij}-function to the LM equation. The L_{ij}-function is defined as follows [5, 6]:

$$L_{ij} = e_{ij} + f_{ij}x_i + g_{ij}P + h_{ij}T \qquad (13)$$

where coefficients e_{ij}, f_{ij}, g_{ij}, h_{ij} are characteristic dimensionless constants of a given binary system [5, 6, 8, 9].

To satisfy the requirement that $L_{ij} = 1$ and $L_{ji} = L_{ij}$ we set [5]

$$\begin{array}{llll} e_{ii}=1 & f_{ii}=0 & g_{ii}=0 & h_{ii}=0 \\ e_{ji}=e_{ij} & f_{ji}=\dfrac{x_i}{x_j}f_{ij} & g_{ji}=g_{ij} & h_{ji}=h_{ij} \end{array} \tag{14}$$

Introducing the L_{ij}-function (eqn. (13)) into the mixing rule (eqn. (8)) for the LM equation yielded the L-LM equation (see Table 2, Figs. 1–3). The values of coefficients e_{ij}, f_{ij}, g_{ij} and h_{ij} of the L-LM equation for all twenty-three binary systems considered were calculated following the method described in our previous work [6], and are presented in Table 3.

The bubble point calculations using the L-LM method were carried out following the approach outlined in ref. 6, that is, first, an initial P value is assumed, then, from this initial P value, using eqn. (13), an initial L_{ij} value can be obtained and the iteration process started. The iteration process needs to be repeated until a preset convergence limit has been reached [6].

Table 2 compares the results of bubble point calculations performed by means of L-LM (this work), L-RKS and L-PR [5], and F-RKS and R-PR [6] methods. Figures 1–3 compare the results of vapor–liquid equilibrium calculations by L-LM methods to the experimental data and the results obtained by the original LM method.

Table 2 and Figs. 1–3 show that the L-LM equation predicts with high accuracy the vapor–liquid equilibrium for all the systems considered. Figures 1–3 also show that introduction of the L_{ij}-function into the mixing rule (eqn. (9)) increases the predictive accuracy of vapor–liquid equilibria markedly. As seen from Table 2, L-LM (this work), L-RKS and L-PR [5], and F-PR [6] methods predict vapor–liquid equilibria of binary mixtures with nearly the same accuracy, although the F-RKS [6] method appears to be slightly more accurate, especially for polar–polar systems.

ACKNOWLEDGMENTS

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

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