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APPLICATION OF L–L MODIFICATION OF VAN DER WAALS EQUATION OF STATE FOR SATURATED BINARY LIQUID MIXTURES

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ABSTRACT

The Law–Lielmezs (L–L) modification of Van der Waals equation of state has been extended to include four hydrocarbon–hydrocarbon binary liquid mixtures for the saturated liquid–vapour equilibrium states. The values of the characteristic mixture p_m and q_m parameters have been calculated, and a relation between the values of these parameters and the molecular weight of binary mixture has been established. The proposed relation is compared with the results obtained by the use of Lielmezs, Howell and Campbell, and Soave 1980 modifications of the Redlich–Kwong equation of state.

INTRODUCTION

Recently, Law and Lielmezs [1] proposed a modification of the Van der Waals equation of state [2] for the saturated liquid–vapour equilibrium states from the triple point up to the critical point. Their modification was developed through the introduction of reduced-state coordinates [3–7] associated with the phenomenological scaling and renormalization group theory [8–11]. The object of this paper is to analyse the predictive applicability of the Law–Lielmezs (L–L) modification of the Van der Waals equation of state in terms of saturated liquid compressibility and vapour pressure data for four hydrocarbon–hydrocarbon binary liquid mixtures, to establish values of the characteristic p_m and q_m parameters and to develop a relation between these parameter values and the molecular weight of the binary mixture.

The proposed correlation is tested by comparing the RMS% error values against the RMS% error values obtained by means of the Lielmezs, Howell and Campbell (L–H–C) and the Soave 1980 modifications of the Redlich–Kwong equation of state [7,12–14].

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TABLE 1

Comparison of results

System [a]	Mole fraction of lighter component	This work				RMS% error			
		Separately calculated		Calculated eqn (13)		Separately calculated		Calculated eqn. (13)	
		p_m	q_m	p_m	q_m	P_m	Z^l_m	P_m	Z^l_m
n-Butane and n-pentane	0.0000	0.365916	0.845910	0.362299	0.849266	1.01	48.14	1.24	48.41
	0.1399	0.376923	0.934736	0.376888	0.920773	0.40	46.83	0.64	46.36
	0.3493	0.382817	0.980303	0.389995	0.986466	0.54	45.75	0.59	45.71
	0.5444	0.385092	0.972401	0.392760	1.002935	0.61	49.00	0.83	49.74
	0.7518	0.399497	0.999687	0.385714	0.973153	0.55	47.50	0.60	47.07
	0.8745	0.385402	0.953887	0.376693	0.932557	0.47	46.37	0.52	45.93
	1.0000	0.352436	0.851596	0.363738	0.873377	0.96	45.08	1.89	45.49
					Average	0.65	46.95	0.90	46.96
n-Butane and n-hexane	0.0000	0.371432	0.805563	0.368078	0.782503	0.70	49.20	1.43	49.21
	0.1035	0.393997	0.953829	0.384829	0.950394	0.56	46.62	0.77	46.83
	0.2841	0.388016	1.097907	0.406028	1.157589	0.99	41.93	1.30	42.76
	0.4928	0.411835	1.272150	0.417799	1.261099	1.20	38.80	1.31	38.48
	0.7017	0.402788	1.227614	0.415912	1.218737	0.98	36.41	1.28	35.95
	0.8127	0.432465	1.154796	0.409345	1.136809	0.56	39.61	0.72	39.76
	0.8980	0.440203	1.094500	0.401676	1.045831	0.42	41.96	0.51	41.64
	1.0000	0.352402	0.851596	0.389504	0.904990	0.96	45.08	5.04	45.76
					Average	0.80	42.45	1.55	42.55
n-Butane and n-heptane	0.0000	0.378996	0.777904	0.362297	0.732655	1.85	52.75	15.39	53.03
	0.1590	0.277408	0.918796	0.294990	0.973020	1.43	44.94	1.91	45.37
	0.4249	0.217519	1.147903	0.241371	1.194902	2.26	34.33	3.06	34.13
	0.6611	0.272650	1.266477	0.250521	1.212003	2.20	28.20	2.42	28.19
	0.8010	0.305627	1.153228	0.291372	1.124331	1.45	30.29	1.53	30.26
	0.9410	0.360628	1.009862	0.347216	0.984123	2.21	37.70	2.26	37.59
	1.0000	0.352436	0.851596	0.377496	0.904714	0.96	45.08	3.46	46.22
					Average	1.77	39.04	4.29	39.26
n-Butane and n-octane	0.0000	0.385255	0.800777	0.345509	0.617486	2.45	56.68	42.18	55.79
	0.1823	0.253525	1.212732	0.329226	1.677508	2.28	45.05	3.99	47.82
	0.4631	0.358304	2.896597	0.322786	2.402367	5.08	28.76	5.57	28.14
	0.6709	0.335407	2.176981	0.332559	2.230230	6.02	24.74	6.07	24.87
	0.8183	0.355999	1.464129	0.347022	1.741800	1.50	21.82	5.11	23.72
	0.9461	0.374175	1.062230	0.364592	1.073066	0.75	31.96	1.21	32.41
	1.0000	0.352436	0.851596	0.373408	0.722558	0.96	45.08	7.00	39.44
					Average	2.72	36.30	10.16	36.03

TABLE 1 (continued)

System [a]	Mole fraction of lighter component	L-H-C method [7,12]				Soave 1980 method [13]			
		RMS% error				Soave coefficients		RMS% error	
		Separately calculated p_m and q_m		Calculated eqn (12) p_m and q_m					
		P_m	Z_m	P_m	Z^1_m	m	n	P_m	Z^1_m
n-Butane and *n*-pentane	0.0000	0.98	21.43	1.22	21.70	0.741122	0.187794	0.16	24.74
	0.1399	0.39	20.83	0.63	20.35	0.610200	0.209980	0.29	21.10
	0.3493	0.53	20.85	0.59	20.82	0.212230	0.472340	0.50	20.82
	0.5444	0.60	25.36	0.93	26.10	0.290144	0.405929	0.55	25.31
	0.7518	0.55	22.27	0.58	21.82	−0.004339	0.669328	0.56	22.20
	0.8745	0.46	21.02	0.51	20.55	0.428829	0.328401	0.36	21.19
	1.0000	0.92	19.74	1.84	20.27	0.658163	0.117830	0.23	22.85
		0.63	21.64	0.90	21.66		Average	0.38	22.60
n-Butane and *n*-hexane	0.0000	0.68	13.76	1.10	13.68	0.753557	0.241179	0.38	13.82
	0.1035	0.55	20.68	0.78	20.93	0.364835	0.383353	0.39	20.85
	0.2841	0.98	16.23	1.41	17.21	−0.379092	0.842841	1.09	15.78
	0.4928	1.20	14.35	1.24	14.14	−1.038540	1.314320	1.20	13.91
	0.7017	0.99	12.33	1.14	12.01	−0.957727	1.275530	0.98	11.94
	0.8127	0.56	15.50	0.82	15.73	−0.965620	1.393880	0.63	15.14
	0.8980	0.42	17.83	0.54	17.56	−0.737342	1.275280	0.49	17.51
	1.0000	0.92	19.74	4.88	20.77	0.658163	0.117830	0.23	22.85
		0.79	16.30	1.49	16.50		Average	0.67	16.48
n-Butane and *n*-heptane	0.0000	1.81	15.41	16.26	15.57	0.813827	0.264283	0.91	16.50
	0.1590	1.40	17.24	1.94	17.96	0.364171	0.192965	1.04	17.28
	0.4249	2.04	8.79	3.06	8.83	−0.235314	0.446540	1.90	8.32
	0.6611	1.88	5.36	2.45	6.10	−0.464836	0.653764	1.80	4.92
	0.8010	1.45	6.72	2.76	5.95	−0.366594	0.679575	1.49	6.24
	0.9410	0.76	12.73	2.27	11.65	0.140459	0.470137	0.70	12.65
	1.0000	0.92	19.74	2.94	20.58	0.658163	0.117830	0.23	22.85
		1.47	12.28	4.53	12.38		Average	1.15	12.68
n-Butane and *n*-octane	0.0000	2.40	29.24	41.26	28.05	0.850820	0.299413	1.11	30.73
	0.1823	2.28	19.41	4.13	22.27	−0.389306	0.600265	1.29	18.90
	0.4631	5.48	4.12	5.64	8.49	−0.839160	0.725660	0.58	4.51
	0.6709	4.30	5.09	5.99	5.56	−0.999315	0.915700	0.85	4.78
	0.8183	1.53	2.95	5.28	3.57	−0.987770	1.09897	1.21(1)	2.91
	0.9461	0.74	9.78	1.21	10.11	−0.232962	0.746975	0.81	9.36
	1.0000	0.92	19.74	7.34	12.54	0.658163	0.117830	0.23	22.85
		2.52	12.90	10.12	12.94		Average	0.88	13.43

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[a] Data taken from Grieves [15], Kay et al (and Thodos) [16–18], Reid et al. [19] and Timmermans [20].

L–L EQUATION EXTENSION TO BINARY MIXTURES

The L–L modification [1] of the Van der Waals equation of state [2] can be extended for binary mixtures as

$$P_{\mathrm{m}} = \frac{RT_{\mathrm{m}}}{V_{\mathrm{m}} - b_{\mathrm{m}}} - \frac{a(T_{\mathrm{m}})}{V_{\mathrm{m}}^2} \tag{1}$$

where coefficient b_{m} may be expressed as

$$b_{\mathrm{m}} = 0.125 \frac{RT_{\mathrm{cm}}}{P_{\mathrm{cm}}} \tag{2}$$

Subscript m represents the state of mixture in terms of lighter component for any given parameter of state. The temperature-dependent $a(T_{\mathrm{m}})$ function is written as:

$$a(T_{\mathrm{m}}) = a(T_{\mathrm{cm}}, P_{\mathrm{cm}})\alpha(T_{\mathrm{m}}^*) \tag{3}$$

Following the work of Lielmezs et al. [1,7,12], the first term of eqn. (3) for binary mixtures may be written as

$$a(T_{\mathrm{cm}}, P_{\mathrm{cm}}) = 0.421875 \frac{R^2 T_{\mathrm{cm}}^2}{P_{\mathrm{cm}}} \tag{4}$$

and the binary mixture temperature-dependent function $\alpha(T_{\mathrm{m}}^*)$ may be defined as

$$\alpha(T_{\mathrm{m}}^*) = 1 + p_{\mathrm{m}}(T_{\mathrm{m}}^*)^{q_{\mathrm{m}}} \tag{5}$$

where p_{m} and q_{m} are characteristic constants of the given binary mixture at constant composition of the lighter component.

The dimensionless binary mixture temperature, T_{m}^*, is given as

$$T_{\mathrm{m}}^* = \frac{(T_{\mathrm{cm}}/T_{\mathrm{m}}) - 1}{(T_{\mathrm{cm}}/T_{\mathrm{NB_m}}) - 1} \tag{6}$$

We rewrite a_{m} and b_{m} as new parameters A_{m} and B_{m}, respectively

$$A_{\mathrm{m}} = 0.421875\ \alpha(T_{\mathrm{m}}^*) \frac{P_{\mathrm{rm}}}{T_{\mathrm{rm}}} \tag{7}$$

$$B_{\mathrm{m}} = 0.125 \frac{P_{\mathrm{rm}}}{T_{\mathrm{rm}}} \tag{8}$$

Substituting A_{m} and B_{m} in eqn. (1), and introducing a binary mixture compressibility factor

$$Z_{\mathrm{m}} = \frac{P_{\mathrm{m}} V_{\mathrm{m}}}{RT_{\mathrm{m}}} \tag{9}$$

yields

$$Z_{\mathrm{m}}^3 - (B_{\mathrm{m}} + 1)Z_{\mathrm{m}}^2 + A_{\mathrm{m}} Z - A_{\mathrm{m}} B_{\mathrm{m}} = 0 \tag{10}$$

The solution of eqn. (10) and, hence, the determination of the values of characteristic binary mixture constants p_m and q_m, are subject to the general requirement that fugacities of the saturated liquid and vapour phases are equal [1,7,12]

$$f_{sm}^{l} = f_{sm}^{v} \tag{11}$$

Accordingly [1,12], the binary mixture fugacity coefficient may be calculated from

$$\ln\frac{f_m}{P_m} = Z_m - 1 - \frac{A_m}{Z_m} - \ln(Z_m - B_m) \tag{12}$$

Using the available experimental data (Table 1), the numerical evaluation of constants p_m and q_m follows the method described by Lielmezs et al. [1,12]. Further generalization of the proposed method follows through correlating the calculated binary mixture characteristic constant values, p_m and q_m, with the binary mixture equivalent molecular weight, MW_m

$$p_m,\ q_m = a' + b'MW_m + c'(MW_m)^2 \tag{13}$$

where constants a', b' and c' characterize the concentration-related molecular weight change for the specified binary mixture in a continuous fashion.

EXPERIMENTAL DATA

Saturated liquid-state volumetric data for the given binary mixtures were taken from several representative sources. The normal boiling point temperatures of mixtures were either taken from direct experimental data listings, or estimated following the procedures outlined by Grieves and Thodos [15]. As these literature data were thought to be sufficiently reliable; no further evaluation of their accuracy was made. The RMS% error is used as a basis for comparison of the accuracy of fit.

DISCUSSION

The calculated results provide a basis for extending the previously proposed modification [1] to binary mixtures. Table 1 presents a comparison between the saturated vapour pressure and liquid state compressibility factor for hydrocarbon–hydrocarbon mixtures obtained in this work and those calculated by the Lielmezs et al. [7,12] and Soave 1980 [13] modifications of the Redlich–Kwong equation of state. The comparison has been made in two ways. First, the results are compared on the basis of separate p_m and q_m values for each binary mixture at each mixture composition. For this method the RMS% errors for pressure are slightly higher for this work than for the

TABLE 2

Polynomial coefficients of eqn. (13)

Mixture	a'	b'	c'
(A) Parameter p_m value vs. equivalent molecular weight of mixture, MW_m			
n-Butane and *n*-pentane	−2.180569	0.079121	−0.000608
n-Butane and *n*-hexane	−0.563306	0.027965	−0.000199
n-Butane and *n*-heptane	2.112968	−0.046968	0.000294
n-Butane and *n*-octane	0.704636	−0.008345	0.000046
(B) Parameter q_m value vs. equivalent molecular weight of mixture, MW_m			
n-Butane and *n*-heptane	−11.103867	0.373457	−0.002880
n-Butane and *n*-hexane	−9.490932	0.302441	−0.002126
n-Butane and *n*-heptane	−4.095163	0.138290	−0.000899
n-Butane and *n*-octane	−13.895393	0.380420	−0.002218

L–H–C method and higher for Soave 1980 results. For liquid-state compressibility factors, Z_m, this method shows considerably higher values than the other two considered methods.

Equation (13) permits, at fixed composition, to connect directly the p_m and q_m values to the corresponding equivalent molecular weight of mixture (Table 2). Indeed, the p_m and q_m parameters calculated from eqn. (13), when inserted into the $\alpha(T_m^*)$ function, yield saturated vapour pressure and liquid compressibility factor values which compare generally well with those obtained by the direct use of p_m and q_m values at fixed concentration. This method, through the use of eqn. (13), introduces the advantage that it can be used for calculation of state properties such as vapour pressure and compressibility factors for mixture compositions where experimental data are not readily available. The proposed extension of Van der Waals equation satisfies the following conditions:

(a) although limited to hydrocarbon–hydrocarbon liquid binary mixtures, the general requirements of the L–L modification of Van der Waals equation have been met [1];

(b) this extension of L–L modification of Van der Waals equation [1] is applicable for calculation of P–V–T relations of binary systems along the saturated liquid–vapour equilibrium states from the triple point up to the critical point.

LIST OF SYMBOLS

a, b	coefficients defined by eqns. (2) and (4) as a function of critical temperature and pressure
a', b', c'	characteristic constants of eqn. (13)
$a(T)$	temperature-dependent parameter of Van der Waals equation defined by eqns. (3) and (5)

A, B	dimensionless parameters introduced by eqns. (7) and (8)
f	fugacity
m, n	coefficients of Soave 1980 method [13]
MW	molecular weight
p	coefficient, defined by eqn. (5)
P	pressure
q	coefficient, defined by eqn. (5)
R	universal gas constant
T	absolute temperature
T^*	dimensionless temperature defined by eqn. (6)
V	volume
Z	compressibility factor

Subscripts

c	critical state
m	state of mixture in terms of higher component
NB	normal boiling point
r	reduced state
s	saturated state

Superscripts

l	liquid phase
v	vapour phase

Greek letters

$\alpha(T_\mathrm{m}^*)$	dimensionless temperature, T^*, dependent parameter, eqns. (3) and (5)

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