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APPLICATION OF L–M MODIFICATION OF THE PENG–ROBINSON EQUATION OF STATE FOR SATURATED BINARY LIQUID MIXTURES

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ABSTRACT

The Lielmezs–Merriman (L-M) modification of the Peng–Robinson equation of state has been extended to saturated liquid mixtures. The values of the characteristic p_m and q_m parameters have been calculated for four hydrocarbon–hydrocarbon liquid mixtures and a relation between the values of these parameters and the molecular weight of the binary mixture has been established. The proposed correlation 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 Lielmezs and Merriman [1] proposed a modification of the Peng–Robinson [2] equation of state for the saturated liquid–vapour equilibrium states from the triple point up to the critical point. Their modification was developed by means of reduced state coordinates [3–5] stemming from the phenomenological scaling and renormalization group theory [6–9]. The object of this note is: first, to study the predictive applicability of the Lielmezs–Merriman modification of the Peng–Robinson equation of state in terms of saturated liquid compressibility and vapour pressure data for the four hydrocarbon–hydrocarbon binary liquid mixtures; second, to establish values of the characteristic p_m and q_m parameters; and third, to develop a relation between those parameter values and the equivalent 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 [4,5] and the Soave-80 [10] modifications of the Redlich–Kwong [11] equation of state.

L–M EQUATION EXTENSION TO BINARY MIXTURES

The L–M modification of the Peng–Robinson equation of state can be extended for binary mixtures as:

$$P_m = \frac{RT_m}{V_m - b_m} - \frac{a(T_m)}{V_m(V_m + b_m) + b_m(V_m - b_m)} \tag{1}$$

where the coefficient b_m is given as:

$$b_m = 0.07780\frac{RT_{cm}}{P_{cm}} \tag{2}$$

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

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

Following the work of Lielmezs et al. [4,5], we write the first term of eqn. (3) for a binary mixture as:

$$a(T_{cm}, P_{cm}) = 0.45724\frac{R^2T_{cm}^2}{P_{cm}} \tag{4}$$

and define the binary mixture temperature-dependent function $\alpha(T_m^*)$ as:

$$\alpha(T_m^*) = 1 + p_m(T_m^*)^{q_m} \tag{5}$$

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:

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

We rewrite a_m and b_m as new parameters A_m and B_m, respectively:

$$A_m = 0.45724\ (T_m^*)\frac{P_{rm}}{T_{rm}^2} \tag{7}$$

$$B_m = 0.97780\frac{P_{rm}}{T_{rm}} \tag{8}$$

Substituting A_m and B_m in eqn. (1), and introducing a binary mixture compressibility factor:

$$Z_m = \frac{P_mV_m}{RT_m} \tag{9}$$

we have:

$$Z^3 - (1 - B_m)Z_m^2 + (A_m - 3B_m^2 - 2B_m)Z_m - (A_mB_m - B_m^2 - B_m^3) = 0 \tag{10}$$

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 thermodynamic requirement that fugacities of the saturated liquid and vapour phases are equal:

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

The binary mixture fugacity coefficient, therefore, may be calculated from Lielmezs et al. [4,5]:

$$\ln \frac{f_m}{p_m} = Z_m - 1 - \ln(Z_m - B_m) - \frac{A_m}{2\sqrt{2}\,B_m} \ln \frac{(Z_m + 2.414B_m)}{(Z_m + 0.414B_m)} \tag{12}$$

The numerical evaluation of the characteristic constants p_m and q_m follows the method described by Lielmezs et al. [4,5].

The proposed method is generalized by correlating the calculated binary mixture characteristic constant, p_m and q_m, values with the binary mixture equivalent molecular weight, MW_m, i.e.:

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

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

EXPERIMENTAL DATA

The saturated binary mixture liquid–vapour equilibrium data were taken from several representative sources (Table 1). These literature data were considered sufficiently reliable. Therefore, no further evaluation of their accuracy was made. The RMS% error is used as a basis for comparison of accuracy of fit (Table 1).

DISCUSSION

The results shown (Table 1) 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 compressibility factor for hydrocarbon–hydrocarbon mixtures obtained in this work and those calculated by Lielmezs et al. [4,5] and Soave [10] modifications of the Redlich–Kwong equation of state.

First, the results have been 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 about the same as those of the L–H–C method [4] and somewhat higher for Soave-80 results. For the liquid state

TABLE 1

Comparison of results

System[a]	Mole fraction of lighter component	This work								L–H–C Method, 1983, 1985				Soave Method, 1980			
						RMS% error				RMS% error						RMS% error	
		Separately calculated		Calculated eqn. (13)		Separately calculated		Calculated eqn. (13)		Separately Calculated		Calculated eqn. (13)		Soave coefficients			
		p_m	q_m	p_m	q_m	P_m	Z^1_m	P_m	Z^1_m	P_m	Z^1_m	P_m	Z^1_m	m_8	n_8	P_m	Z^1_m
n-Butane	0.0000	0.303806	0.865897	0.299422	0.866505	0.79	11.61	1.17	11.77	0.98	21.43	1.22	21.70	0.741122	0.187794	0.16	24.74
and	0.1399	0.306113	0.951686	0.308092	0.941953	0.34	9.19	0.57	8.85	0.39	20.83	0.63	20.35	0.610200	0.209980	0.29	21.10
n-pentane	0.3493	0.309660	1.006265	0.315776	1.011481	0.48	9.54	0.55	9.51	0.53	20.85	0.59	20.82	0.212230	0.472340	0.50	20.82
	0.5444	0.311144	0.996959	0.317207	1.029287	0.55	16.32	0.77	16.80	0.60	25.36	0.93	26.10	0.290144	0.405929	0.55	25.31
	0.7518	0.326171	1.030694	0.312674	0.998564	0.54	10.99	0.59	10.47	0.55	22.27	0.58	21.82	−0.004339	0.669320	0.56	22.20
	0.8745	0.312633	0.974823	0.307050	0.956263	0.40	9.70	0.45	9.31	0.46	21.02	0.51	20.55	0.428829	0.328401	0.36	21.19
	1.0000	0.289725	0.872172	0.299038	0.894458	0.71	10.14	1.60	10.71	0.92	19.74	1.84	20.27	0.658163	0.177830	0.23	22.85
					Average	0.54	11.07	0.81	11.06	0.63	21.64	0.90	21.66		Average	0.38	22.60
n-Butane	0.0000	0.311015	0.829727	0.303580	0.789159	0.59	3.65	3.00	3.57	0.68	13.76	1.10	13.68	0.753557	0.241179	0.38	13.82
and	0.1035	0.321792	0.978853	0.318337	0.991010	0.48	9.35	0.79	9.78	0.55	20.68	0.78	20.93	0.364835	0.383353	0.39	20.85
n-hexane	0.2841	0.316846	1.159464	0.336909	1.239466	0.94	5.48	1.29	6.27	0.98	16.23	1.41	17.21	−0.379092	0.842841	1.09	15.78
	0.4928	0.346298	1.390506	0.346992	1.362143	1.23	4.44	1.35	4.28	1.20	14.35	1.24	14.14	−1.038540	1.314320	1.20	13.91
	0.7017	0.336278	1.329708	0.344865	1.308341	0.99	4.02	1.28	4.03	0.99	12.33	1.14	12.01	−0.963631	1.280383	0.98	11.95

	0.8127	0.358716	1.221392	0.338761	1.207869	0.55	4.93	0.73	5.00	0.56	15.50	0.82	15.73	−0.965620	1.393880	0.63	15.14
	0.8980	0.361123	1.138030	0.331724	1.096763	0.40	6.59	0.48	6.34	0.42	17.83	0.54	17.56	−0.737342	1.275280	0.49	17.51
	1.0000	0.289725	1.872172	0.320627	0.925128	0.71	10.14	4.56	11.28	0.92	19.74	4.88	20.77	0.658163	0.177830	0.23	22.85
					Average	0.74	6.08	1.69	6.32	0.79	16.30	1.49	16.50		Average	0.67	16.48
n-Butane	0.0000	0.319625	0.798717	0.302438	0.728763	0.71	10.14	19.41	4.03	1.81	15.41	16.26	15.57	0.813827	0.264283	0.91	16.50
and	0.1590	0.217381	0.955245	0.236498	1.049624	1.27	6.07	1.91	7.07	1.40	17.24	1.94	17.96	0.364171	0.192965	1.04	17.28
n-heptane	0.4249	0.161092	1.294242	0.183151	1.340990	2.26	5.50	3.04	5.78	2.04	8.79	3.06	8.83	−0.199672	0.421456	2.09	8.40
	0.6611	0.213195	1.437862	0.190779	1.355988	2.30	9.73	2.40	9.70	1.88	5.36	2.45	6.10	−0.456637	0.647686	1.75	5.83
	0.8010	0.243097	1.256306	0.229240	1.229806	1.43	6.86	1.58	6.75	1.45	6.72	2.76	5.92	−0.366594	0.679575	1.49	6.24
	0.9401	0.291606	1.046830	0.282362	1.033340	2.15	4.38	2.21	4.29	0.76	12.73	2.27	11.65	0.069383	0.526480	4.61	11.64
	1.0000	0.289725	0.872172	0.311257	0.922826	0.71	10.14	3.19	11.48	0.92	19.74	2.94	20.58	0.658163	0.177830	0.23	22.85
					Average	1.55	7.55	4.83	7.01	1.47	12.28	4.53	12.38		Average	1.30	12.68
n-butane	0.0000	0.326394	0.820752	0.246945	0.415639	2.19	23.56	117.93	22.70	2.40	29.24	41.26	28.05	0.850819	0.299413	1.19	30.73
and	0.1823	0.191764	1.356836	0.434279	2.578500	2.32	7.29	4.58	9.66	2.28	19.41	4.13	22.27	−0.389305	0.600263	1.29	18.90
n-octane	0.4631	0.921271	5.752381	0.555264	4.017615	5.97	10.34	6.60	10.60	5.48	4.12	5.64	8.49	−0.520298	0.487133	1.29	8.88
	0.6707	0.338114	3.049890	0.514031	3.605807	5.61	10.58	5.62	10.50	4.30	5.09	5.99	5.56	−0.891713	0.834937	0.99	5.61
	0.8183	0.303458	1.702011	0.417157	2.550074	1.71	11.50	5.52	10.05	1.53	2.95	5.28	3.57	−0.987770	1.098974	1.21	2.91
	0.9461	0.305659	1.116686	0.287907	1.123583	0.69	5.46	1.58	5.21	0.74	9.78	1.21	10.11	−0.232962	0.746975	0.81	9.36
	1.10600	0.289725	0.872172	0.220758	0.379245	0.71	10.14	15.31	7.42	0.92	19.74	7.34	12.54	0.658163	0.177830	0.23	22.85
						2.74	11.27	22.45	10.88	2.52	12.90	10.12	12.94		Average	1.00	14.18

[a] Data taken from refs. 12–17.

TABLE 2

Polynomial coefficients of eqn. (13)

Mixture	a'	b'	c'
(A) Parameter p_m value versus equivalent molecular weight of mixture, MW_m			
n-Butane and *n*-pentane	−1.248840	0.048063	−0.000369
n-Butane and *n*-hexane	−0.535565	0.025076	−0.000178
n-Butane and *n*-heptane	1.979373	−0.045225	0.000284
n-Butane and *n*-octane	−2.524422	0.071025	−0.000409
(B) Parameter q_m value versus equivalent molecular weight of mixture, MW_m			
n-Butane and *n*-pentane	−11.670218	0.391926	−0.003024
n-Butane and *n*-hexane	−11.677092	0.366326	−0.002572
n-Butane and *n*-heptane	−5.939443	0.189222	−0.001224
n-Butane and *n*-octane	−30.353686	0.797466	−0.004623

compressibility factor, Z_m^1, this method shows smaller RMS% error values than the other two considered methods.

Second, the use of eqn. (13) permits p_m and q_m values at fixed composition to be directly connected to the corresponding equivalent molecular weight of mixture (Table 2). 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 excellently with those obtained by the direct use of p_m and q_m values at fixed concentration. 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. Although presently applied to hydrocarbon–hydrocarbon liquid binary mixtures, the proposed method satisfies the general requirements of the L–M modification [1] of the Peng–Robinson equation.

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NOMENCLATURE

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 the Peng–Robinson 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 [10]
p, q	coefficients, defined by eqn. (5)
P	pressure
MW	molecular weight
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

$\alpha(T_m^*)$	dimensionless temperature T^*-dependent parameter, eqns. (3) and (5)

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