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SATURATED VAPOUR–LIQUID EQUILIBRIA CALCULATION WITH MODIFIED MARTIN EQUATION OF STATE

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ABSTRACT

L–H–C type temperature function has been introduced into the Martin equation of state. This modification has been used to calculate over the entire liquid range for pure substances, the saturated liquid and vapor compressibilities and the saturated pressure. A comparison has been made for a series of pure substances (17 compounds, 407 data points pairs) with the results obtained by means of this work and by the use of Martin I, II and III equation forms, the Soave 1972 and 1980, and the L–H–C modifications of the Redlich–Kwong equation, and the generalized parameter technique of Panagiotopoulos and Kumar applied to the Redlich–Kwong equation of state.

THE MARTIN EQUATION OF STATE

Martin [1] indicated that the three constant form of the Clausius equation of state [2] is the best of the available two term cubic equations in the volume, i.e.:

$$P=\frac{RT}{V-b}-\frac{a(T)}{(V+c)^2} \tag{1}$$

where a, b and c are the substance dependent parameters of the equation of state. Martin rewrote eqn. (1) in the reduced form of corresponding states as:

$$P_r=\frac{T_r}{Z_cV_r-B}-\frac{A(T_r)}{(Z_cV_r+c)^2} \tag{2}$$

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TABLE 1

Comparison of results of this work with experiment and other calculation methods [1,3–5,9–11]

Compound	This work					L–H–C		
	Constants		RMS%			RMS%		
	p	q	P	Z_g	Z_l	P	Z_g	Z_l
iso-Butane	0.17635989	0.36663151	0.82	7.92	4.34	0.96	5.54	17.65
n-Butane	0.07779350	0.30862600	0.89	5.71	8.45	0.92	4.93	19.74
tert-Butanol	0.15648152	0.48992181	0.68	6.76	5.65	1.40	7.82	9.42
CS_2	0.29385600	0.15136500	0.45	2.19	3.55	2.65	7.08	6.78
Ethane	0.10026700	0.35049600	1.08	5.56	7.55	1.07	5.55	14.78
Ethanol	0.55545928	0.39459735	3.04	2.30	27.25	3.87	8.97	17.83
n-Hexane	0.35400862	0.61885798	0.53	1.94	13.09	0.68	7.14	13.76
n-Hydrogen	0.05918685	0.35540402	0.35	1.00	5.05	2.95	50.11	54.44
p-Hydrogen	0.075071573	0.28687435	0.42	3.49	4.57	2.98	50.05	53.49
H_2S	0.14922887	0.09883249	0.24	1.51	0.43	1.25	3.58	6.17
Methanol	0.59716091	0.44417620	4.21	7.09	42.07	2.81	13.56	36.31
Neon	0.18602952	0.35061795	0.64	8.76	6.44	1.02	2.81	4.71
Iso-pentane	0.079101801	0.33595788	0.26	5.88	8.15	0.71	6.62	19.62
n-Pentane	0.20751637	0.45033938	0.32	11.17	7.42	0.98	6.76	21.43
Neo-pentane	0.14772099	0.39199418	0.29	8.13	5.02	0.76	5.10	17.16
Water	0.56763200	0.4344933	5.69	7.32	34.68	6.13	8.36	37.70
Xenon	0.18580639	0.30172247	0.63	3.89	3.02	0.92	4.42	6.40
Average RMS% error value [a]			1.21	5.33	10.98	1.89	11.67	21.02

Compound	Martin I, II, III RMS%											
	Data			P			Z_g			Z_l		
	ω	N_I	N_{II}, A, B	I	II	III	*I*	II	III	I	II	III
iso-Butane	0.176	0.97		1.12		1.10	4.87		7.12	14.41		17.55
n-Butane	0.193	1.0		1.09		1.10	4.59		5.62	14.75		17.42
tert-Butane	0.618	1.85		3.21		1.20	3.53		5.70	21.68		15.49
CS_2	0.115	1.0		0.62		0.58	2.64		8.91	6.05		9.17
Ethane	0.098	0.679	0.7, 1.0, 8.0	1.21	1.34	1.12	3.19	12.25	3.64	15.08	12.35	15.74
Ethanol	0.635	2.25		6.35		2.95	5.16		5.29	36.31		26.58
n-Hexane	0.296	1.135	1.0, 5.0, 7.0	1.03	2.78	0.58	6.62	10.43	4.64	15.54	24.36	13.06
n-Hydrogen	−0.22	0.14		0.51		0.42	3.57		2.32	8.09		6.26
p-Hydrogen	−0.22	0.13		0.62		0.54	3.57		3.61	8.09		8.02
H_2S	0.100	0.58		0.45		0.40	1.09		1.12	4.78		4.06
Methanol	0.559	1.55		5.33		3.75	6.93		7.26	47.33		41.07
Neon	0.000	0.43		1.03		0.95	4.32		4.19	10.96		10.63
Iso-pentane	0.227	0.97		0.43		0.40	3.00		6.19	12.79		17.45
n-Pentane	0.251	1.0	1.0, 5.0, 8.0	1.25	2.78	0.83	11.86	10.43	9.22	17.20	24.36	17.62
Neo-pentane	0.197	0.79		0.41		0.32	2.99		2.48	14.82		14.74
Water	0.344	1.165	0.95, 3.0, 8.0	5.88	7.22	3.78	3.88	5.93	4.50	37.96	45.31	33.57
Xenon	0.002	0.47		0.92		0.69	6.33		3.77	5.64		6.24
Average RMS% error value [a]				1.85	3.53	1.22	4.60	9.76	5.03	17.15	26.60	16.16

TABLE 1 (continued)

Compound	Soave I, II RMS%						*P-K* Parameter application RMS%		
	P		Z_g		Z_l				
	I	II	I	II	I	II	P	Z_g	Z_l
iso-Butane	1.02	0.15	8.29	7.80	21.14	20.26	0.19	19.53	0.38
n-Butane	1.10	0.23	7.88	7.52	23.91	22.85	0.19	17.91	0.22
tert-Butanol	1.70	0.83	8.79	8.55	10.59	10.14	0.26	13.21	0.39
CS_2	4.41	0.59	8.59	8.03	9.44	8.30	0.38	11.21	3.08
Ethane	0.90	0.23	6.69	6.71	18.97	18.11	0.17	13.63	0.29
Ethanol	6.28	2.19	8.97	8.97	17.82	17.83	0.40	18.83	0.35
n-Hexane	1.33	0.38	7.17	7.15	14.00	13.82	0.34	15.89	0.57
n-Hydrogen	11.70	0.66	49.92	49.97	54.31	54.27	0.24	5.20	1.10
p-Hydrogen	12.17	0.84	49.64	49.68	53.23	53.17	0.24	5.95	0.50
H_2S	1.03	0.12	3.59	3.58	6.28	6.26	0.35	1.77	0.10
Methanol	10.42	0.95	13.57	13.56	36.17	36.32	0.44	27.17	0.14
Neon	9.25	0.30	2.82	2.91	5.71	5.42	0.18	6.37	0.72
Iso-pentane	0.99	0.42	9.33	8.92	24.30	23.35	0.18	21.43	0.41
n-Pentane	0.96	0.16	9.09	8.73	25.76	24.74	0.88	21.78	0.23
Neo-pentane	0.68	0.26	5.97	5.75	20.50	19.90	0.14	17.01	0.45
Water	11.57	0.55	9.92	9.65	40.32	39.73	0.43	21.26	0.17
Xenon	1.20	0.25	4.45	4.43	7.01	6.78	0.28	8.74	0.31
Average RMS% error value [a]	4.51	0.54	12.63	12.47	22.91	22.43	0.31	14.52	0.59

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[a] RMS% is defined with respect to the experiment as: RMS% error $= \left[\frac{1}{N}\Sigma(\%\ error)_i^2\right]^{1/2}$ where, for instance, for saturated pressure % error $= \left(\frac{P_{\text{exp}} - P_{\text{calc}}}{P_{\text{exp}}}\right) \times 100.$

where:

$A = aP_c/R^2T_c^2$

$B = bP_c/RT_c$

$C = cP_c/RT_c$

and Z_c is the experimental compressibility factor at the critical point.
To fit data along the critical isotherm, following Martin [1] and Joffe [3], we write:

$$A = 27/64T_r^N \tag{3a}$$

$$B = 0.857Z_c - 0.1674 \tag{3b}$$

$$C = 0.1250 - B \tag{3c}$$

Putting relations (3a–3c) into eqn. (2) yields the "original Martin equation of state", or $\mathbf{M}_\mathrm{I}$ (Table 1). This equation of state fits the results for reduced temperatures from $T_r \approx 0.8$ up to $T_r = 2.0$. Below $T_r = 0.8$, the temperature function T_r^N (parameter A, eqn. (3a), see also ref. 4) may be modified to a new expression, $T_r^N - \alpha\, e^{-\beta T_r}$. If this modification:

$$A(T_r) = \frac{27/64}{T_r^N - \alpha \exp(-\beta T_r)} \tag{4a}$$

$$B = 0.857Z_c - 0.1674 \tag{4b}$$

$$C = 0.1250 - B \tag{4c}$$

in which parameters B and C have been kept the same, is introduced into eqn. (2), we have the modified Martin equation of state [4], or $\mathbf{M}_\mathrm{II}$ (Table 1):

$$P_r = \frac{T_r}{Z_cV_r - B} - \frac{27/64}{[(T_r^N - \alpha \exp(-\beta T_r))](Z_cV_r + C)^2} \tag{5}$$

Following the work of Martin [1] and later Joffe [3], we modified eqn. (2) by replacing the term T_r^N in eqn. (3a) by the Soave (1972) [5] temperature function α^*:

$$\alpha^* = 1.0 + m(1.0 - T_r) \tag{6}$$

in which $m = 0.480 + 1.574\omega - 0.176\omega^2$, and ω is the Pitzer acentric factor [6–8]. This modification of the Martin equation was then identified as $\mathbf{M}_\mathrm{III}$ (Table 1).

PROPOSED MODIFICATION

Following the method of Lielmezs et al. [9], the temperature dependent function, $a(T)$, of eqn. (1) is rewritten as:

$$a(T) = a(T_c, P_c)\alpha(T^*) \tag{7}$$

in which:

$$a(T_c, P_c) = \frac{27}{64}\frac{R^2T_c^2}{P_c} \tag{8}$$

and:

$$\alpha(T^*) = 1 + pT^{*q} \tag{9}$$

such that p and q are the characteristic constants of a substance at its saturated liquid–vapour equilibrium state, while T^* is defined as:

$$T^* = \left(\frac{T_c}{T} - 1\right)\Bigg/\left(\frac{T_c}{T_{NB}} - 1\right) \tag{10}$$

The calculation of the values of the constants p and q is subject to the general thermodynamic restraint of saturated vapour–liquid equilibrium; i.e., the fugacities of liquid and vapour phases are equal (Lielmezs et al. [9]):

$$f_s^l = f_s^v \tag{11}$$

Putting the newly introduced expressions, eqns. (7–10), into eqns. (3a–3c), we obtain:

$$D(0.857Z_c - 0.1674)(P_r/T_r) \tag{12}$$

$$E = (0.2924 - 0.857Z_c)(P_r/T_r) \tag{13}$$

$$F = \frac{27}{64}\frac{P_r}{T_r^2}\alpha(T^*) \tag{14}$$

We now rewrite eqn. (1) in terms of the compressibility factor Z by means of parameters D, E and F (eqns. (12–14)) as:

$$Z^3 + (2E - D - 1)Z^2 + (F - 2DE - 2E + E^2)Z - (FD + DE^2 + E^2) = 0 \tag{15}$$

On the other hand, if we subject eqn. (1) to the general thermodynamic requirement:

$$\ln\frac{f}{P} = \int_0^P\left(\frac{V}{RT} - \frac{1}{P}\right)\mathrm{d}P \tag{16}$$

and introduce eqn. (5), we obtain the fugacity coefficient of pure substances for the Martin equation of state in terms of the proposed modification, (eqns. (7–10)):

$$\ln\frac{f}{P} = \ln\frac{1}{Z - D} = \frac{D}{Z - D} - \frac{2F}{Z + E} + \frac{FE}{(Z + E)^2} \tag{17}$$

Equation (15) is solved for the saturated vapour, Z_s^v and saturated liquid, Z_s^l, compressibility factors, while eqns. (11–14, 17) are used to calculate the corresponding fugacity coefficients, f_s^v and f_s^l. The numerical evaluation of constants p and q follows the method described by Lielmezs et al. [9].

EXPERIMENTAL DATA

The physical property and saturated liquid–vapour equilibrium data utilized (Table 1) were taken from the sources as listed by Lielmezs et al. [9]. These data were thought to be sufficiently reliable. The RMS% error is used as a basis for comparison of the accuracy of fit (Table 1).

RESULTS AND DISCUSSION

The introduction of a temperature-dependent function, $\alpha(T^*)$ (eqns. 7–10), into the a term of the Martin equation of state (eqn. 1) allows the calculation of saturated vapour pressures and the vapour and liquid compressibilities (Table 1) for pure compounds from the triple point to the vapour–liquid critical point. Table 1 presents, in terms of RMS% error, a comparison between the results obtained from this work, experimental data and those calculated by using the Martin **I**, **II** and **III** equations [1, 3, 4], the L–H–C [9], the Soave 1972 and 1980 equations [5, 10] and the Panagiotopoulos and Kumar [11] generalized parameter method. When the results of the six methods (excluding the method of Panagiotopoulos and Kumar) are compared (Table 1), it is found that the present work gives the most accurate results for saturated liquid compressibilities, with the $\mathbf{M}_{\mathrm{III}}$ method second, and the $\mathbf{M}_{\mathrm{I}}$ method third. For saturated vapour compressibilities, the $\mathbf{M}_{\mathrm{I}}$ method is the most accurate, the $\mathbf{M}_{\mathrm{III}}$ method the second and this work the third most accurate. For saturated vapour pressures, the Soave **III** (1980) gives the lowest RMS% error; this work is seen to be the second best followed by the $\mathbf{M}_{\mathrm{III}}$ method.

The apparently excellent results of the generalized technique of Panagiotopoulos and Kumar (Table 1) result from the fact that for each temperature the corresponding saturated liquid molar volumes and the saturation pressures are the required input data; that is, these fitted values of saturation pressures and saturated liquid state compressibility factors are back-calculated values of the input experimental data.

Following the calculation procedures already established by Lielmezs et al. [9], the proposed modification of the Martin equation satisfies the following conditions:

(1) There is a new temperature-dependent function, $\alpha(T^*)$, which has two adjustable parameters, p and q. It is suggested that p and q values be determined from the available saturated liquid equilibrium data. The required normal boiling and liquid–vapour critical point temperatures are usually available.

(2) The new temperature-dependent function, $\alpha(T^*)$ (eqns. 7–10), becomes unity at the critical state:

$$\alpha(T^*) \to 1.0$$
$$T \to T_c$$

and the proposed modification of the Martin equation satisfies the necessary conditions at the critical point.

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LIST OF SYMBOLS

a, b, c	coefficients defined by eqns. (1) and (2)
$a(T)$	temperature dependent parameter, defined by eqn. (7)
A, B, C	parameters introduced by eqns. (2) and (3a–3c)
D, E, F	parameters introduced by eqns. (12–14)
f	fugacity
m	coefficient introduced by eqn. (6)
N	coefficient to be calculated, eqn. (3a)
p	coefficient, defined by eqn. (9)
P	pressure
q	coefficient, defined by eqn. (9)
R	universal gas constant
T	absolute temperature
T^*	dimensionless temperature, defined by eqn. (10)
V	volume
Z	compressibility factor

Subscripts

c	critical state
g	gas state
l	liquid state
NB	normal boiling point
r	reduced state
s	saturated state

Superscripts

l	liquid phase
v	vapour phase

Greek letters

α, β	coefficients introduce y eqn. (4a)
α^*	temperature depender unction, defined by eqn. (6)
$\alpha(T^*)$	dimensionless temper re, T^*, dependent function, defined by eqn. (9)
ω	acentric factor

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