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USE OF MODIFIED MARTIN EQUATION FOR UNSATURATED VAPOUR AND LIQUID STATES

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ABSTRACT

The Chakma–Lielmezs–Islam modification of the Martin equation of state

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

where

$$a(T)=a(P_c, T_c)\alpha(T^*)$$

in which

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

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

has been extended to unsaturated liquid and vapour states by means of a correcting function C_f, such that the $\alpha(T^*)$ term becomes

$$\alpha(T^*)=1+pC_fT^{*q}$$

The proposed extension has been successfully compared with the results obtained by means of the original Martin equation of state, the Chakma–Lielmezs–Islam modification of the Martin equation for the saturated states, and the Soave-1972 modification of the Redlich–Kwong equation of state.

LIST OF SYMBOLS

a, b, c	coefficients defined by eqns. (1), (2) and (3)
$a(T)$	temperature dependent parameter, defined by eqn. (4)
C_f	correcting function defined by eqn. (16)
D, E, F	parameters introduced by eqns. (9), (10) and (11)

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f	fugacity
m, n	coefficient introduced by eqn. (6)
N	coefficient found in the original Martin equation [2]
p	coefficient, defined by eqn. (6)
P	pressure
q	coefficient, defined by eqn. (6)
R	universal gas constant
RMS	root mean square
T	absolute temperature
T^*	dimensionless temperature, defined by eqn. (7)
V	volume
Z	compressibility factor

Subscripts

c	critical state
exp	experimental
f	correcting function, eqn. (16)
h	identified dimensionless T and P, defined by eqns. (17), (18)
NB	normal boiling point
r	reduced state
s	saturated state

Superscripts

l	liquid phase
v	vapour phase

Greek letter

$\alpha(T^*)$	dimensionless temperature, T^*, dependent function, defined by eqn. (6)

INTRODUCTION

Recently Chakma, Lielmezs and Islam [1] proposed a modification of the Martin equation of state [2–5] for the saturated liquid–vapour equilibrium states. The present work extends this modification into the unsaturated vapour and liquid region at and below the critical isotherm and isobar. This is achieved by introducing a correction term C_f as a linear function of temperature and pressure with which the saturated vapour–liquid equilibrium curve is related to the given unsaturated state of the fluid.

The proposed correlation is tested by comparing the RMS% error values of this work, against the RMS%-error values obtained by means of the original Martin equation of state [2,4], the Chakma–Lielmezs–Islam (C–L–I) modification of the Martin equation for saturated states [1], and the Soave-1972 modification of the Redlich–Kwong equation of state [6] for compressibility factor values of 12 compounds with 481 data points in their unsaturated vapour state and for 12 compounds with 444 data points in the unsaturated liquid state.

EXTENSION TO UNSATURATED FLUID STATES

The Chakma–Lielmezs–Islam (C–L–I) modification of the Martin equation of state [1] is

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

where

$$b=(0.857Z_c-0.1674)\left(\frac{RT_c}{P_c}\right) \tag{2}$$

$$c=(0.2924-0.857Z_c)(RT_c/P_c) \tag{3}$$

and

$$a(T)=a(T_c,\ P_c)\alpha(T^*) \tag{4}$$

in which

$$a(T_c,\ P_c)=(27/64)(R^2T_c^2/P_c) \tag{5}$$

and

$$\alpha(T^*)=1+pT^{*q} \tag{6}$$

with T^* defined as

$$T^*=[(T_c/T)-1]/[(T_c/T_{NB})-1] \tag{7}$$

where parameters p and q are characteristic constants of the substance at its saturated vapour–liquid equilibrium state. Equation (1) may be written in terms of the compressibility factor Z as

$$Z^3+(2E-D-1)Z^2+(F-2DE-2E+E^2)Z-(FD+DE^2+E^2)=0 \tag{8}$$

where

$$D=(0.857Z_c-0.1674)(P/P_c)(T_c/T) \tag{9}$$

$$E=(0.2924-0.857Z_c)(P/P_c)(T_c/T) \tag{10}$$

$$F=(27/64)(P/P_c)(T_c/T)^2\alpha(T^*) \tag{11}$$

Equation (1) with eqns. (2–7) must satisfy the thermodynamic requirement that

$$\ln\left(\frac{f}{P}\right) = \int_0^P \left(\frac{V}{RT} - \frac{1}{P}\right) \mathrm{d}P \tag{12}$$

When eqn. (7) is applied to eqn. (12), we see that

$$\ln(f/P) = \mathrm{func}(Z, D, E, F) \tag{13}$$

The univariance of the saturated vapour–liquid equilibrium system assures that chemical potentials of vapour and liquid phases are equal. If so, the fugacities correspondingly are equal; i.e.

$$f_s^{\mathrm{l}} = f_s^{\mathrm{v}} \tag{14}$$

The numerical evaluation of the constants p and q (eqn. 6) subject to the restraint of eqn. (14) at the saturated vapour–liquid equilibrium, and designated as p_s and q_s follows the method developed by Lielmezs, Howell and Campbell [7] and had been taken from reference [1]. In order to extend the Chakma, Lielmezs and Islam modification of the Martin equation to the unsaturated vapour and liquid states we introduce a new, linear in temperature and pressure, correcting function, C_f, so that the $\alpha(T^*)$-term in eqn. (6) becomes

$$\alpha(T^*) = 1 + p_s C_f T^{*q_s} \tag{15}$$

The new correcting function C_f, is expressed in terms of a dimensionless temperature, T_h, and dimensionless pressure P_h as

$$C_f = 1 + mT_h + nP_h \tag{16}$$

in which

$$T_h = \left.\frac{|T_{\mathrm{exp}} - T_s|}{T_s}\right|_P \tag{17}$$

and

$$P_h = \left.\frac{|P_{\mathrm{exp}} - P_s|}{P_s}\right|_T \tag{18}$$

Coefficients m and n of eqn. (16) are constants characteristic of a given pure compound while subscript exp (eqns. 17, 18) represents the experimental (thermodynamic state) temperature and pressure, respectively. The term, T_s, eqn (17) is defined as the temperature which would be found on the saturated vapour–liquid equilibrium curve for the given state pressure, P_{exp}. Similarly, the term P_s (eqn. 18) represents the pressure which would be located on the saturated vapour–liquid equilibrium curve for the given state temperature, T_{exp}.

To calculate the values of coefficients m and n (Table 1), the value of the correcting function C_f (eqn. 16) was found for each state. This calculation was done by means of eqn. (1) and the associated relations eqns. (2–14) of the C–L–I modification of the Martin equation [1] using unsaturated state data (Table 1), p_s and q_s values taken as noted from ref. 1, and setting the initial value of $C_f = 1$, in eqns. 15, 16. The values of terms T_h (eqn. 17) and P_h (eqn. 18) were calculated using saturated liquid–vapour equilibrium data (Table 1) by means of the Aitken's interpolation method. If the saturated liquid–vapour equilibrium data are not readily available, the T_s and P_s values required may be calculated by means of the C–L–I modification of the Martin equation [2,4] for saturated states, or independently, by means of a saturated vapour pressure–temperature relation such as the Harlacher–Braun equation [8]. Using the calculated C_f, P_h and T_h values, coefficients m and n (eqn. 16) were determined by means of non-linear regression, minimizing the sum of squares of errors between the experimental value of the compressibility factor Z_{exp} and the calculated value, Z_{calc} (Table 1).

DATA USED

The P–V–T data of saturated and unsaturated states were taken from several representative sources (Table 1). All p_s and q_s values (eqn. 6) were taken from the work of Chakma, Lielmezs and Islam [1]. The RMS%-error in compressibility factor Z was used as a basis of comparison of accuracy of fit.

RESULTS AND DISCUSSION

The calculated results provide a basis for extending the already proposed C–L–I modification of the Martin equation to unsaturated vapour and liquid states below the critical isotherm and the critical isobar. Table 1 presents a comparison in terms of RMS% error between the unsaturated vapour and liquid state compressibilities for this work and those calculated by the original Martin equation [2,4], the C–L–I modification of the Martin equation for the saturated states [1], and the Soave-1972 modification of the Redlich–Kwong equation of state [6]. Of all the equations of state compared, this work (Table 1) exhibited the best overall behaviour, both in vapour and liquid states. The only exceptions were the behaviour of ethane and neopentane in the vapour state, and n-hexane in the liquid state, for which the Soave-1972 modification of the Redlich–Kwong equation performed better. The proposed extension satisfies the general requirements of the C–L–I modification of the Martin equation of state.

TABLE 1

Data used and comparison of results

Compound	N No. of data points	Reference	Coefficient "N" Martin eqn. [2,4]	Coefficient eqns. (16–18)		RMS % error in Z			
				m	n	This work	Martin eqn. [2,4]	C–L–I modification of Martin eqn. [1]	Soave eqn. 1972 [6]
			Vapour state						
Ethane	101	11	0.679	−17.747010	5.544424	3.40	6.48	5.90	2.40
n-Butane	53	9	1.0	0.013777	−3.210167	3.21	12.02	11.23	3.88
i-Butane	65	15	0.97	52.522020	−12.765630	3.56	13.53	12.75	4.86
n-Pentane	32	11	1.0	37.228585	−8.843183	2.67	9.11	7.85	2.84
neopentane	28	16	0.79	23.839310	−6.917596	4.61	10.05	9.14	2.60
tert. Butanol	65	12	1.135	−7.145245	9.839694	1.84	2.80	3.59	4.13
n-Hydrogen	19	11	0.14	−0.963490	0.190041	0.36	11.62	11.47	1.10
p-Hydrogen	20	11	0.13	8.768921	−3.853640	1.53	11.59	11.40	1.78
Neon	18	11	0.43	−1.764376	1.335245	0.70	2.11	1.40	1.24
H_2S	22	14	0.58	−13.137815	4.104375	0.78	0.81	0.99	0.93
Water	23	18	1.165	7.289599	−2.783190	1.84	1.19	1.54	2.05
Average						2.23	7.39	7.02	2.54
			Liquid state						
Ethane	52	17	0.679	3.607845	−0.012204	4.76	95.95	95.17	15.45
n-Butane	36	11	1.0	5.827861	−0.055675	4.96	93.11	91.07	11.94
i-Butane	65	11	0.97	1.606140	0.009753	2.59	88.85	87.14	12.73
n-Pentane	63	11	1.0	−0.519141	−0.046359	10.05	85.70	82.49	14.17
neopentane	46	16	0.79	−23.08313	1.060152	5.11	91.01	89.28	11.86
n-Hexane	61	11	1.135	3.181320	−0.097525	25.47	79.90	73.81	18.25
n-Hydrogen	19	11	0.14	3.443763	−0.443940	2.46	98.08	98.02	7.64
p-Hydrogen	46	11	0.13	−3.480635	−0.027889	2.67	97.42	97.34	10.20
Neon	26	11	0.43	7.77082	−0.036679	1.88	96.56	96.36	5.20
H_2S	14	13	0.58	0.348715	−0.026181	0.39	95.94	95.22	7.21
Water	40	18	1.165	−5.999829	0.014848	21.87	82.16	69.39	36.74
Average						7.47	91.33	88.65	13.76

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