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MODIFIED VAN DER WAALS EQUATION OF STATE FOR SATURATED VAPOUR–LIQUID EQUILIBRIUM

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ABSTRACT

Defining the dimensionless temperature T^* as

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

the attractive pressure term of Van der Waals equation of state has been modified by introducing a new temperature-dependent function

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

The new modified Van der Waals equation predicts the saturated liquid–vapour states satisfactorily over the whole range of investigation from the triple point to the critical point. A comparison was made with experimental data for a series of selected fluids (19 compounds, 447 data point pairs) and results obtained by the use of Van der Waals and Redlich–Kwong equations, and Lielmezs, Howell and Campbell, and Soave modifications of the Redlich–Kwong equations of state.

INTRODUCTION

In this work the temperature dependence of the attractive force term of the Van der Waals equation of state [1] is introduced by means of a newly proposed reduced temperature T^* term [2], associated with the phenomenological scaling and renormalization group theory [3–6]. This reduced temperature T^* term is expressed as a function of temperature T, the normal boiling point temperature T_{NB}, the critical point temperature T_c and two substance-dependent constants, p and q, derived from saturated vapour–liquid equilibrium data. The proposed modification of the Van der Waals equation predicts the saturated liquid–vapour equilibrium states for the types of liquids studied with an improved accuracy over the entire range of investigation from the triple point up to the critical point.

PROPOSED MODIFICATION

The Van der Waals equation of state is

$$P=\frac{RT}{V-b}-\frac{a}{V^2} \tag{1}$$

If we let the characteristic constants, a and b, be functions of the critical state variables, T_c and P_c, then we have

$$a=a(T_c, P_c)$$
$$b=b(T_c, P_c) \tag{2}$$

If we further apply to eqns. (1) and (2) the critical state thermodynamic criteria for stability

$$\left(\frac{\partial P}{\partial V}\right)_{T_c}=0;\quad \left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c}=0 \tag{3}$$

we obtain for a one-component system

$$a(T_c, P_c)=\frac{27R^2T_c^2}{64P_c} \tag{4a}$$

$$b(T_c, P_c)=\frac{RT_c}{8P_c} \tag{4b}$$

If, on the other hand, we let parameter a be temperature dependent, we may define it as a product of two terms (compare with Lielmezs et al. [2])

$$a(T)=a(T_c, P_c)\alpha(T^*) \tag{5}$$

where the $\alpha(T^*)$ function has been introduced by Lielmezs et al. [2] as

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

in which p and q are characteristic curve-fitting constants of a given pure substance along the saturated liquid–vapour equilibrium states, but T^* is defined as [2]

$$T^*=\left(\frac{T_c}{T}-1\right)\Big/\left(\frac{T_c}{T_{NB}}-1\right) \tag{7}$$

where T, T_c, and T_{NB} are temperatures, in K, of the given state, the critical point and the normal boiling point, respectively. Substituting eqn. (5) into eqn. (1) we obtain the modified form, this work, of the Van der Waals equation of state

$$P=\frac{RT}{V-b}-\frac{a(T_c, P_c)\alpha(T^*)}{V^2} \tag{8}$$

The modified Van der Waals equation of state (eqn. 8) may be equivalently re-written in terms of compressibility factor Z as

$$Z^3-(B+1)Z^2+AZ-AB=0 \tag{9}$$

in which

$$A = \frac{a(T)P}{R^2T^2} = \frac{27P_r\alpha(T^*)}{64T_r} \tag{10}$$

and

$$B = \frac{bP}{8T} = \frac{P_r}{8T_r} \tag{11}$$

where the reduced pressure, $P_r = P/P_c$, and the reduced temperature, $T_r = T/T_c$. Equation (9) is subject to the general thermodynamic requirement

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

Combining eqns. (9) and (12), we have

$$\ln\frac{f}{P} = Z - 1 - \frac{A}{Z} - \ln(Z - B) \tag{13}$$

Since the saturated equilibrium curves represent states of coexistence of pairs of phases (i.e., liquid–vapour) and the system is thermodynamically univariant, we can say that for a pure substance at saturated state at a given temperature T and for a given value of *a(T)*, a single value of P exists for which the chemical potentials of both phases, liquid and vapour are equal as are fugacities, i.e.

$$f_s^{\mathrm{L}} = f_s^{\mathrm{V}} \tag{14}$$

Consequently, from eqn. (14) it follows that a necessary and sufficient condition of the saturated vapour–liquid equilibrium is that along the saturation curve the compressibilities of each phase yield equal values of the fugacity coefficient when substituted into eqn. (13).

Equation (9) is solved for the compressibility factors, Z^{V} and Z^{L}; and eqn. (13) is used to calculate the fugacity coefficients, f_s^{V} and f_s^{L}, subject to relation (14). If the fugacity coefficients for the two saturated phases are not within a special tolerance limit, the $\alpha(T^*)$ function value is slightly changed; thus changing the value of the parameter A and repeating the process of calculation until condition (14) is met, i.e., the fugacity coefficient f^{L} had approached the value of f^{V} within the specified tolerance range assuring that the desired value of the $\alpha(T^*)$ function is uniquely defined. Using non-linear regression methods it is now possible to obtain the p and q values for each of the given pure substances.

EXPERIMENTAL DATA USED

Table 1 gives a summary of experimental data used. These saturated vapour–liquid equilibrium data were considered to be of sufficient reliabil-

TABLE 1

Summary of experimental data used

Compound	Critical pressure (atm)	Critical density (g cm^{-3})	Critical temp. (K)	Normal boiling temp. (K)	Reduced temp. range	Pitzer factor (31)	No. of data points	Ref.
Benzene	48.59(9)	0.3045	561.83	353.25	0.486–1.00	0.212	17	9, 10
Isobutane	36.0	0.221	408.13	261.32	0.640–1.00	0.176	31	11
n-Butane	37.47	0.228	425.16	272.67	0.641–1.00	0.193	33	11
Tertiary butanol	41.77	0.2584	508.87	356.48	0.701–1.00	0.618	13	12
Carbon disulfide	75.19	0.3682	546.15	319.37	0.500–1.00	0.115	27	13
Deuterium	16.43	0.0699	38.35	23.66	0.482–0.99	−0.13	23	14
Ethane	48.20	0.2056	305.42	184.47	0.604–1.00	0.098	24	15
Ethyl alcohol	63.0	0.2762	516.15	351.443	0.592–1.00	0.635	17	15
Hexane	29.94	0.233	507.86	342.16	0.612–1.00	0.296	15	16
Hydrogen	12.98	0.0149	33.18	20.380	0.420–1.00	−0.22	21	14
para-Hydrogen	12.759	0.0156	32.976	20.268	0.419–1.00	−0.22	22	17
Hydrogen sulfide	88.2(8)	0.3460	373.07	212.875	0.518–1.00	0.100	30	8
Methyl alcohol	78.5	0.2717	513.15	337.696	0.532–1.00	0.559	17	15
Neon	26.19	0.4835	44.40	27.09	0.563–1.00	0.00	21	18
Isopentane	33.37	0.236	460.39	301.025	0.654–1.00	0.227	29	11
n-Pentane	33.25	0.237	469.65	309.19	0.658–1.00	0.251	29	11
Neopentane	31.545	0.232	433.75	282.628	0.652–1.00	0.197	27	11
Water	218.3	0.3155	647.3	373.15	0.422–1.00	0.344	37	19
Xenon	57.6	1.099	289.74	165.02	0.570–1.00	0.002	14	20

TABLE 2

Comparison of results for pure compounds tested

Compound	This work					Van der Waals		
	p	q	RMS% error			RMS% error		
			P	Z^L	Z^V	P	Z^L	Z^V
Benzene	0.4395614982	0.0000100000	52.28	47.85	11.41	81.86	68.04	12.41
CS_2	0.3462708911	0.7098963453	2.72	38.42	9.48	58.89	57.73	14.75
Ethane	0.3140700049	0.8155646276	1.11	39.68	11.03	34.29	59.15	17.81
Ethanol	0.5609743674	0.7682665765	3.88	58.81	12.66	87.01	84.66	12.94
H_2S	0.3428953309	0.7691206071	1.28	39.86	6.21	61.63	54.44	7.42
Isobutane	0.3414939763	0.8514247741	0.99	12.49	12.49	32.49	21.38	21.38
Isopentane	0.3557228569	0.8426635030	0.74	45.30	13.38	35.28	66.90	21.88
Methanol	0.5514769463	0.7328093636	2.82	83.73	17.69	85.09	112.33	18.07
n-Butane	0.3524356125	0.8515963578	0.96	45.08	11.39	32.96	66.85	19.90
n-Hexane	0.3714324019	0.8055633315	0.70	49.20	10.96	63.88	71.36	11.99
n-Pentane	0.3659163895	0.8459103371	1.01	48.14	13.13	38.13	70.70	21.09
Deuterium	0.1063189310	0.6114444513	1.93	22.31	11.67	31.52	30.14	15.02
Neon	0.1957767194	0.7369182712	1.08	27.89	6.38	38.90	40.28	9.07
Neopentane	0.3375202099	0.8485090082	0.79	42.46	10.74	35.07	63.52	17.78
n-Hydrogen	0.0481190038	0.2922359962	3.00	40.88	49.13	19.82	39.22	48.49
P-Hydrogen	0.0454488385	0.3046920680	3.02	39.97	48.93	18.33	38.06	48.01
t-Butanol	0.5218597181	0.8896193291	1.42	39.77	12.70	53.85	71.84	18.51
Water	0.5228298469	0.7180295424	6.21	81.89	12.28	71.41	112.42	17.02
Xenon	0.2596411384	0.7612780718	0.96	35.91	8.27	46.15	48.69	9.77
Av. RMS% error			4.57	44.19	15.29	48.77	61.98	19.12

TABLE 2 (continued)

Compound	Lielmezs–Howell–Campbell			Soave-1980		
	RMS% error			RMS% error		
	P	Z^L	Z^V	P	Z^L	Z^V
Benzene	51.98	10.21	9.37	116.69	15.70	9.73
CS_2	2.65	6.78	7.08	0.59	8.30	8.03
Ethane	1.07	14.78	5.55	0.23	18.11	6.71
Ethanol	3.87	17.83	8.97	2.19	17.83	8.97
H_2S	1.25	6.17	3.58	0.12	6.26	3.58
Isobutane	0.96	17.65	5.54	0.15	20.26	7.80
Isopentane	0.71	19.62	6.62	0.42	23.35	8.92
Methanol	2.81	36.31	13.56	0.95	36.32	13.56
n-Butane	0.92	19.74	4.93	0.23	22.85	7.52
n-Hexane	0.68	13.76	7.14	0.38	13.82	7.15
n-Pentane	0.98	21.43	6.76	0.16	24.74	8.73
Deuterium	1.84	6.53	7.56	0.15	6.95	8.17
Neon	1.02	4.71	2.81	0.30	5.42	2.91
Neopentane	0.76	17.16	5.10	0.26	19.90	5.75
n-Hydrogen	2.95	54.44	50.11	0.66	54.27	49.97
p-Hydrogen	2.98	53.49	50.05	0.84	53.17	49.50
t-Butanol	1.40	9.42	7.82	0.83	10.14	8.55
Water	6.13	37.70	8.36	0.55	39.73	9.65
Xenon	0.92	6.40	4.42	0.25	6.78	4.43
Av. RMS% error	4.52	19.69	11.33	6.63	21.26	12.09

TABLE 3

Comparison of results of average RMS% error for compound groups

Group	This work			Van der Waals			Lielmezs–Howell–Campbell			Soave-1980		
	P	Z^L	Z^V	P	Z^L	Z^V	P	Z^L	Z^V	P	Z^L	Z^V
Aromatic	52.28	47.85	11.93	81.56	68.04	12.41	51.98	10.21	9.37	116.69	15.70	9.73
Simple fluids	1.02	31.90	7.33	42.53	44.49	9.42	0.97	5.57	3.62	0.28	6.10	3.66
Sulphur compounds	2.00	39.14	7.84	60.26	56.09	11.09	1.95	6.47	5.33	0.35	7.28	5.80
Quantum fluids	2.65	34.39	36.58	23.23	35.81	37.17	2.59	38.16	35.91	0.55	38.13	35.88
H-bonded compounds	3.58	66.05	13.83	74.34	95.31	16.63	3.55	25.31	9.68	1.13	26.00	10.18
Paraffins	0.90	40.34	11.87	38.87	59.98	18.83	0.87	17.73	5.95	0.26	20.43	5.95

ity, and we did not make any further studies to re-evaluate their accuracy. The presently used data set, therefore, is only a representative one. The RMS% error (Tables 2 and 3) is used as a basis for comparison introducing a measure of accuracy of fit for this work and the Van der Waals equation of state [1], the Lielmezs, Howell and Campbell modification of the Redlich–Kwong equation [2] and the Soave-1980 relation [7].

RESULTS AND DISCUSSION

The introduction of temperature dependence by means of the proposed $\alpha(T^*)$ function (eqns. 5–8) into the a-term of the Van der Waals equation of state (eqns. 1 and 8) has permitted us to calculate the saturated state vapour pressures and vapour and liquid state compressibilities (Tables 2 and 3) for pure compounds along the entire liquid range from the triple point up to the vapour–liquid critical point.

The introduced $\alpha(T^*)$ function modifies the Van der Waals equation without directly referring to the nature of the saturated vapour–liquid equilibrium, the type and magnitude of the intermolecular forces involved and the molecular structure of the fluids present. Instead the proposed

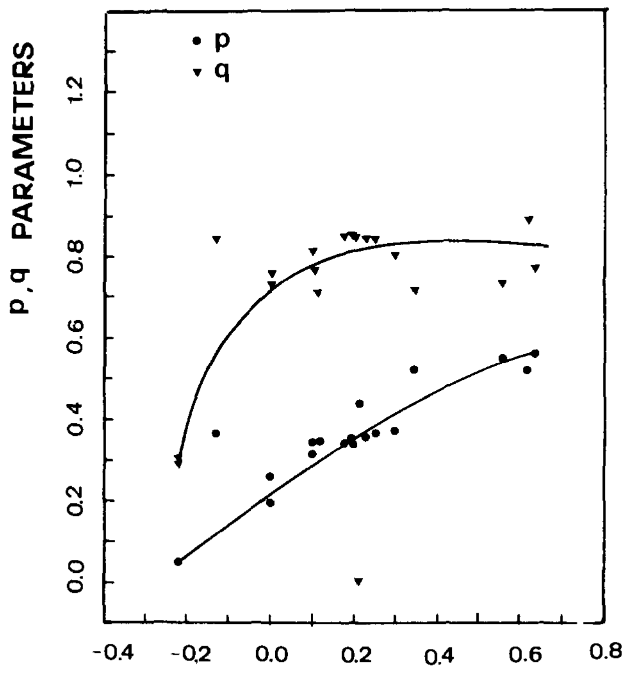

Fig. 1. The p and q parameter plot versus the Pitzer acentric factor, ω.

method requires the knowledge of the vapour–liquid critical point temperature and pressure, the normal boiling point temperature and the two empirical, substance dependent constants p and q, determined from the available saturated liquid–vapour equilibrium data. If the experimental data needed are not readily available, Fig. 1 implies that it may be possible to express the $\alpha(T^*)$ function constants p and q through the Pitzer acentric factor ω (Table 1). As seen from this figure, the parameter q tends to converge to a constant value of $q \approx 0.81$, and appears to be scarcely dependent on ω, i.e., it is not affected to a large extent by the intermolecular forces. On the other hand, parameter p tends to correlate with ω (Fig. 1). For a given 19 compounds by means of non-linear regression techniques, the following p–ω correlation was obtained

$$p = 0.229 + 0.814\omega - 0.486\omega^2 \tag{15}$$

with correlation variance of 0.001449. Table 2 compares the results, in the form of RMS% error, for this work, the original Van der Waals equation [1], the Lielmezs, Howell and Campbell (LHC) modification of the Redlich–Kwong equation [2] and the Soave-1980 relation [7]. Table 3, by means of RMS% error estimates, compares the results of the 19 compounds tested separated into the following compound groups:

Paraffins: isobutane, *n*-butane, ethane, hexane, isopentane, *n*-pentane, neopentane
H-bonded: tertiary butanol, ethyl alcohol, methyl alcohol, water
Quantum fluids: deuterium, hydrogen, parahydrogen
Simple fluids: neon, xenon
Sulphur compounds: carbon disulfide, hydrogen sulfide
Aromatic: benzene

Tables 2 and 3 indicate that the proposed modification of the Van der Waals equation is significantly better than the original Van der Waals equation for calculating all three properties considered: saturation state vapour pressure, P, and vapour and liquid compressibilities, Z^V and Z^L. However, in an overall estimate, when compared with the LHC and Soave-1980 modifications of the Redlich–Kwong equation of state, as expected, both these modifications show significantly better results for all three properties (P, Z^L and Z^V) considered either for separate pure compounds (Table 2) or for compound groups (Table 3) than the modified Van der Waals equation, this work.

Following the calculation procedures already established by Lielmezs et al. [2], the proposed modification of the Van der Waals equation, this work, satisfies the conditions listed below.

(a) It has two adjustable, substance-characteristic parameters, p and q, of which p can be expressed as a non-linear relation of the Pitzer acentric factor (eqn. 15).

Presently, it is suggested that p and q values be determined from the available saturated liquid–vapour equilibrium data. The normal boiling point temperatures are considered to be available.

(b) The new attractive force $\alpha(T^*)$ function (eqns. 5–8) is temperature dependent, and it becomes unity at the critical state, i.e.

$$\alpha(T^*) \rightarrow 1.0 \quad \text{when } T \rightarrow T_c \tag{16}$$

so that the proposed modification of the Van der Waals equation of state, this work, satisfies the necessary conditions at the critical point.

The results obtained (Tables 2 and 3) strongly support the proposed modification of the Van der Waals equation.

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NOMENCLATURE

a, b	Van der Waals equation coefficients which are functions of critical temperature and pressure
$a(T)$	temperature dependent parameter of the Van der Waals equation of state, eqn. (5)
$a(T_c, P_c)$	coefficient, eqn. (4a)
$b(T_c, P_c)$	coefficient, eqn. (4b)
A, B	dimensionless parameters, eqns. (10) and (11)
f	fugacity coefficient
p, q	coefficients, eqns. (6) and (7)
P	pressure (atm)
R	universal gas constant
RMS	root mean square
T	absolute temperature (K)
T^*	reduced dimensionless temperature, eqn. (7)
V	volume
Z^L	liquid compressibility factor
Z^V	vapour compressibility factor

Subscripts

c	critical state
r	reduced

s	saturated
NB	normal boiling point

Superscripts

L	liquid phase
V	vapour phase

Greek Letters

$\alpha(T^*)$	dimensionless temperature-dependent function, eqns. (5)–(8)
ω	Pitzer's acentric factor

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