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APPLICATION OF MODIFIED REDLICH–KWONG EQUATION FOR UNSATURATED VAPOUR AND LIQUID STATES

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ABSTRACT

The Lielmezs–Howell–Campbell modification of the Redlich–Kwong equation of state

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

where

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

and

$$\alpha(T^*)=1+p(T^*)^q$$

has been extended to include unsaturated states in terms of a correcting function C_f such that the $a(T^*)$ term becomes

$$\alpha(T^*)=1+pC_f(T^*)^q$$

A comparison has been made for pure substances in the vapour state (14 compounds, 1330 data point pairs) and in the liquid state (12 compounds, 827 data point pairs) with the results obtained by means of this work and the Soave 1972 modification of the Redlich–Kwong equation and Lee–Kesler equation of state.

INTRODUCTION

This work extends the recent saturated state modifications of the Redlich–Kwong equation of state for pure substances [1] and binary mixtures [2] to include unsaturated vapour and liquid regions at and below the critical isotherm and isobar. This is done by introducing a temperature and pressure dependent term C_f relating the saturated vapour–liquid equilibrium curve to the given unsaturated state of the fluid.

The correlation is tested by comparing the RMS % error values of this work, against the RMS % error values obtained by means of the Soave modification of the Redlich–Kwong equation [3] and the Lee–Kesler equation of state [4] for volumes for 14 compounds with 1330 data points in their unsaturated vapour state and for volumes of 12 compounds with 877 data points in the unsaturated liquid state.

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L–H–C equation extension to unsaturated fluid states

The L–H–C modification of the Redlich–Kwong equation of state is [1]

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

where

$$a(T)=a(T_c, P_c)\alpha(T^*) \tag{2}$$

$$b=0.08664\frac{RT_c}{P_c} \tag{3}$$

with

$$a(T_c, P_c)=0.42748\frac{R^2T_c^2}{P_c} \tag{4}$$

and

$$\alpha(T^*)=1+p(T^*)^q \tag{5}$$

in which T^* is defined as

$$T^*=\frac{[(T_c/T)-1]}{[(T_c/T_{NB})-1]} \tag{6}$$

while parameters p and q are characteristic constants of the substance at its saturated vapour–liquid equilibrium state.

We rewrite a and b (eqns. 2–5) as new parameters

$$\begin{aligned} A&=0.42748\alpha(T^*)\frac{P_r}{(T_r)} \\ &=0.42748[1+p(T^*)^q]\frac{P_r}{(T_r)^2} \end{aligned} \tag{7}$$

$$B=0.08644\frac{P_r}{T_r} \tag{8}$$

Putting A and B into eqn. (1) we obtain a cubic equation for the compressibility factor, Z

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

The L–H–C modification of the Redlich–Kwong equation must satisfy the thermodynamic requirement that

$$\ln\left[\frac{f}{P}\right]=\int_0^P\left[\frac{V}{RT}-\frac{1}{P}\right]\mathrm{d}P \tag{10}$$

Applying eqn. (9) to eqn. (10), we obtain

$$\ln\left[\frac{f}{P}\right]=Z-1-\ln(Z-B)-\frac{A}{B}\left[1+\frac{B}{Z}\right] \tag{11}$$

For the univariant saturated vapour–liquid equilibrium the chemical potentials of vapour and liquid phases are equal. Therefore we write for the fugacities

$$f^{L}_{sat} = f^{V}_{sat} \tag{12}$$

The numerical evaluation of the constants p and q (eqn. 5), subject to the restrain of eqn. (12) at the saturated vapour–liquid equilibrium state, designated as p_{sat} and q_{sat}, follows the method described by Lielmezs et al. [1]. To extend the L–H–C modification of the R–K equation to the unsaturated vapour and liquid states, we introduce a new correction function C_f, linear in temperature and pressure, so that the $\alpha(T^*)$ term (eqn. 5) becomes

$$\alpha(T^*) = 1 + p_{sat}C_f(T^*)^{q_{sat}} \tag{13}$$

We express the new correction function, C_f, in terms of dimensionless temperature, T_h, and dimensionless pressure, P_h as

$$C = 1 + mT_h + nP_h \tag{14}$$

where

$$T_h = \left.\frac{|T_{exp} - T_{sat}|}{T_{sat}}\right|_P \tag{15}$$

$$P_h = \left.\frac{|P_{exp} - P_{sat}|}{P_{sat}}\right|_T \tag{16}$$

Coefficients m and n of eqn. (14) are constants characteristic of a given pure compound while subscript exp (eqns. 15 and 16) represents the experimental (thermodynamic state) temperature and pressure, respectively. The term T_{sat} (eqn. 15) 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_{sat} (eqn. 16) represents the pressure which would be located on the saturated vapour–liquid equilibrium curve for the given state temperature, T_{exp}.

The coefficients m and n (Table 1) were determined by multiple linear regression techniques using a set of calculated C_f, P_h and T_h values. Calculation of C_f was performed employing eqn. (1) and associated conditions (eqns. 2–12) using unsaturated state, P, V and T data and assuming that initially $C_f = 1$ at the saturated state. Coefficients p_{sat} and q_{sat} of eqn. (13) were taken from ref. 1 and T_h and P_h values (eqns. 15 and 16) were calculated using saturated liquid–vapour equilibrium data by means of Aitken's interpolation method. For the case where saturated liquid–vapour equilibrium data are not readily available, the necessary P_{sat} and T_{sat} values may be calculated by the method suggested in ref. 1 or independently by means of a saturated vapour-pressure–temperature relation such as the Harlacher–Braun equation [5].

TABLE 1

Data used and comparison of results

Compound	Data used							Comparison of results					
	Normal boiling point, T_{NB}(K)	Critical state		Pitzer's acentric factor	Data used range		Number of data points	Data ref.	m	n	RMS % error in volume		
		Temperature T_c(K)	Pressure P_c (atm)		ΔT_r	ΔP_r					This work	Soave 1972	Lee-Kesler
Vapours													
Methane	111.42	190.55	45.81	0.008	0.525–0.997	0.0043-0.862	130	6	−5.5593	0.06144	0.42	0.19	0.30
Ethane	184.52	305.5	48.49	0.098	0.665–0.982	0.0203-0.814	100	6	−0.5401	−1.0794	0.61	1.28	0.50
Propane	231.11	370.00	42.08	0.152	0.662–0.973	0.0023-0.821	131	6	5.1483	1.5489	0.94	1.35	0.40
n-Butane	272.67	425.16	37.47	0.193	0.659–0.997	0.0267-0.961	53	8	−3.8905	−2.4223	1.27	2.49	0.73
n-Pentane	309.19	469.65	33.29	0.251	0.660–0.979	0.0301-0.842	32	14	−1.9924	−1.6450	1.11	3.01	0.20
n-Hexane	341.89	507.87	29.92	0.296	0.678–0.995	0.0023-0.910	148	12	−10.5075	−8.0976	2.40	3.52	1.43
Methanol	338.0	513.15	78.46	0.559	0.660–0.985	0.00086-0.867	56	15	−10.8458	−0.1151	2.22	4.61	1.83
t-Butanol	356.49	508.87	41.77	0.618	0.720–0.993	0.0239-0.570	76	13	137.8980	21.3010	4.59	4.32	2.52
Water	373.15	647.30	218.31	0.344	0.453–0.978	0.000045-0.678	409	10	1.1282	−0.8948	0.50	1.14	0.33
H_2S	212.88	373.54	90.05	0.100	0.743–0.922	0.0112-0.459	37	11	−2.4812	−1.4568	1.18	1.14	1.03
n-Hydrogen	20.38	33.23	12.99	−0.22	0.662–0.963	0.0760-0.760	19	6	−7.4422	−1.9496	0.85	1.51	8.88
p-Hydrogen	20.28	32.98	12.76	−0.22	0.667–0.970	0.0773-0.773	20	6	−17.1898	−7.0703	1.64	1.72	9.02
Neon	27.09	44.4	26.19	0.00	0.563–0.901	0.0038-0.377	18	6	−5.2834	−3.2110	0.73	1.07	0.91
Argon	87.29	150.86	49.35	−0.004	0.002–0.900	0.597-0.994	101	6	−3.3464	−1.4002	0.59	0.84	0.59
Average											1.36	2.01	2.05
Liquids													
Methane	111.47	190.55	45.81	0.008	0.499–0.945	0.0043-0.862	156	6	−0.5260	−0.00366	2.32	2.89	1.29
Propane	231.11	370.00	42.08	0.152	0.622–0.919	0.0235-0.938	119	6	−7.4221	−0.06333	4.55	11.63	1.82
n-Butane	272.67	425.16	37.47	0.193	0.690–0.925	0.527-0.790	16	6	−15.0783	−0.2565	7.71	17.83	2.06
n-Pentane	309.19	469.65	33.29	0.251	0.624–0.837	0.296-0.889	24	6	−8.8691	−0.03333	3.61	16.61	1.78
n-Hexane	341.87	507.87	29.92	0.296	0.676–0.951	0.330-0.990	23	6	−13.7112	−0.1036	5.93	21.18	1.86
Methanol	338.0	513.15	78.46	0.559	0.581–0.953	0.0647-0.836	46	9, 15	−103.6491	−0.1415	14.55	52.93	12.74
Water	373.15	647.30	218.31	0.344	0.422–0.978	0.000045-0.904	256	10	3.2736	−0.00014	53.48	42.59	19.20
H_2S	212.88	373.54	90.05	0.100	0.743–0.922	0.153-0.957	17	7, 10, 11	−12.1263	−0.4312	3.79	8.23	1.66
n-Hydrogen	20.38	33.23	12.99	−0.22	0.434–0.993	0.0762-0.912	45	6	15.8307	0.01885	7.41	16.41	29.32
p-Hydrogen	20.28	32.98	12.76	−0.22	0.424–0.970	0.0773-0.928	46	6	15.3688	0.00360	4.06	14.38	8.19
Neon	27.09	44.4	26.19	0.00	0.563–0.901	0.0377-0.942	26	6	3.0077	0.00754	2.09	5.25	6.48
Argon	87.29	150.86	49.35	−0.004	0.563–0.994	0.02-1.00	103	6	0.8629	−0.00766	2.97	4.13	3.46
Average											9.37	17.84	7.49

Data used

The $P-V-T$ data of saturated and unsaturated states were taken from several representative sources listed in Table 1. All p_{sat} and q_{sat} values (eqn. 5) were taken from the paper by Lielmezs and co-workers [1]. All these data were thought to be sufficiently reliable. Therefore, no further assessment of their accuracy was made. The RMS % error is used as a basis of comparison of the accuracy of fit.

RESULTS AND DISCUSSION

Lielmezs et al. [1] discussed the theoretical assumptions regarding the L–H–C modification of the Redlich–Kwong equation of state for pure compounds along the saturated vapour–liquid equilibrium curve. The calculated results provide a basis for extending the previously proposed L–H–C modification of the Redlich–Kwong equation to unsaturated liquid and vapour states at and below the critical isotherm and the critical isobar. Table 1 presents in terms of RMS % error a comparison between the unsaturated vapour and liquid state volume values obtained from this work and those calculated by the Soave 1972 modification of the Redlich–Kwong equation [3] and the Lee–Kesler equation of state [4]. Of the two cubic equations of state compared, this work exhibits better behaviour for both vapour and liquid states, than the Soave 1972 modification of the R–K equation. As expected, the more complex Lee–Kesler equation gives the lowest RMS % error for all volumes, except for the quantum fluids, n- and p-hydrogen. The proposed method satisfies the general requirement of the L–H–C modification of the R–K equation [1].

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NOMENCLATURE

a, b	coefficients defined by eqns. (1–4) as a function of critical temperature and pressure
$a(T)$	temperature dependent parameter of the Redlich–Kwong equation defined by eqns. (1) and (2)
A, B	dimensionless parameter introduced by eqns. (7) and (8)

C_f	correcting function defined by eqn. (14)
f	fugacity
m, n	coefficients, defined by eqn. (14)
P	pressure
p, q	coefficients defined by eqn. (5)
R	universal gas constant
RMS	root mean square
T	absolute temperature
T^*	dimensionless temperature, defined by eqn. (6)
V	volume
Z	compressibility factor

Subscripts

c	critical state
exp	experimental
f	correcting function, eqn. (14)
h	identifies dimensionless T and P, defined by eqns. (15) and (16)
NB	normal boiling point
r	reduced state
rs	reduced saturated state
sat	saturated

Superscripts

L	liquid state
V	vapour state

Greek notation

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

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