*Thermochimica Acta*, 105 (1986) 383–389
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

# MODIFICATION OF PENG–ROBINSON EQUATION OF STATE FOR SATURATED VAPOUR–LIQUID EQUILIBRIUM

J. LIELMEZS and L.H. MERRIMAN

*Department of Chemical Engineering, The University of British Columbia, Vancouver, B.C. (Canada)*

(Received 6 February 1986)

The Peng–Robinson [1] modification of the Redlich–Kwong [2] equation of state has in recent years been widely used in chemical engineering [3] for predicting the vapour–liquid equilibria and volumetric properties. In this work, the temperature-dependent attractive force term of the Peng–Robinson equation is modified by a new proposed reduced temperature term, $T^*$, introduced by Lielmezs et al. [4]. This term is associated with the phenomenological scaling and renormalization group theory by Griffiths [5], Kadanoff [6], Wegner [7] and Wilson and Kogut [8]. This reduced temperature term, $T^*$, is expressed as a function of temperature $T$, the normal boiling point $T_{NB}$, the critical point temperature $T_C$ and two substance-dependent constants $p$ and $q$, derived from saturated vapour–liquid equilibrium data. The proposed modification predicts the saturated liquid–vapour equilibrium states for all types of liquids accurately over the entire liquid range from the triple point up to the critical point. The presented correlation is tested by comparing the RMS% error values against the RMS% error values obtained by using Peng–Robinson [1], Lielmezs et al. [4] and Soave [13] modifications of the Redlich–Kwong equation.

## PROPOSED MODIFICATION

The Peng–Robinson modification of the Redlich–Kwong equation of state is:

$$p = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+b(V-b)} \tag{1}$$

where coefficients at the critical state may be expressed as:

$$a(T_C) = 0.45724\frac{R^2T_C^2}{P_C} \tag{2}$$

$$b(T_C) = 0.07780\frac{RT_C}{P_C} \tag{3}$$

$$Z_C = 0.307 \tag{4}$$

0040-6031/86/$03.50

For temperatures other than the critical state, Peng and Robinson [1] suggested:

$$a(T) = a(T_C) \times \alpha(T_r, \omega) \tag{5}$$

$$b(T) = b(T_C) \tag{6}$$

where $\alpha(T_r, \omega)$ is a dimensionless function of reduced temperature and Pitzer's acentric factor, $\omega$, and equals unity at the critical temperature.

If eqn. (1) is rewritten as:

$$Z^3 - (1 - B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0 \tag{7}$$

where

$$A = \frac{a(T)P}{R^2T^2} \tag{8}$$

$$B = \frac{bP}{RT} \tag{9}$$

$$Z = \frac{PV}{RT} \tag{10}$$

and subjected to the thermodynamic relation:

$$\ln\frac{f}{P} = \int_0^P \left(\frac{V}{RT} - \frac{1}{P}\right) \mathrm{d}P \tag{11}$$

then the following relation for the fugacity $f$ of a pure component is obtained:

$$\ln\frac{f}{P} = Z - 1 - \ln(Z - B) - \frac{A}{2\sqrt{2}B}\ln\frac{Z + 2.414B}{Z - 0.414B} \tag{12}$$

To modify the presented Peng–Robinson equation of state we rewrite eqn. (5) as follows:

$$a(T) = a(T_C) \times \alpha(T^*) \tag{13}$$

To express the $\alpha(T^*)$ term of eqn. (13) as a continuous, temperature-dependent function, the previously proposed reduced $T^*$-coordinate [4,9–11] is introduced, where $T^*$ is defined as:

$$T^* = \left(\frac{T_C}{T} - 1\right) \bigg/ \left(\frac{T_C}{T_{NB}} - 1\right) \tag{14}$$

where $T$, $T_C$ and $T_{NB}$ are the temperatures (K) of the given state, the critical point and the normal boiling point, respectively.

The $\alpha(T^*)$ temperature dependence may now be written in terms of $T^*$ as:

$$\alpha(T^*) = 1 + pT^{*q} \tag{15}$$

where $p$ and $q$ are characteristic constants of a given pure substance. Equation (15) is taken along the saturated liquid–vapour equilibrium curve.

The determination of the values of characteristic substance parameters, $p$ and $q$, is subject to the general thermodynamic restraint of saturated vapour–liquid equilibrium; that is, the fugacities of liquid and vapour phases are equal [4]:

$$f_s^L = f_s^V \tag{16}$$

where s represents the saturation state and L and V are the liquid and vapour states, respectively. To determine the value of the $\alpha(T^*)$ function from eqns. (14) and (15), parameters $A$ and $B$ are calculated as:

$$A = \frac{a(T_C)\alpha(T^*)P}{R^2T^2} = \frac{0.45724P_r\alpha(T^*)}{T_r^2} \tag{17}$$

$$B = \frac{b(T_C)P}{RT} = \frac{0.07780P_r}{T_r} \tag{18}$$

Equation (7) is then solved for the compressibility factors, $Z^V$ and $Z^L$; and eqns. (12), (16)–(18) are used to calculate the fugacity coefficients, $f^V$ and $f^L$. The numerical evaluation of the parameters $p$ and $q$ follows the method described by Lielmezs et al. [4].

## EXPERIMENTAL DATA

The saturated liquid–vapour equilibrium data were taken from several representative sources. These literature data were thought to be 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).

## RESULTS AND DISCUSSION

The introduction of a temperature-dependent, $\alpha(T^*)$, function (eqns. 13, 14 and 15) into the attractive force-dependent $a$-term of the Peng–Robinson modification of the Redlich–Kwong equation (eqns. 1 and 5) allows the calculation of the saturated vapour pressures and the vapour and liquid state compressibilities (Table 1) 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 original Peng–Robinson equation without any direct statement regarding the nature of the saturated vapour–liquid equilibrium, the type and magnitude of the intermolecular forces, and the understanding of the molecular structure of the fluids involved. Instead the proposed method requires the knowledge of vapour–liquid critical point temperature and pressure, the normal boiling point temperature and the two empirical, substance-dependent constants $p$

TABLE 1

Comparison of results

| Compound [a] | This work | | | | | Peng–Robinson | | | Lielmezs–Howell–Campbell | | | Soave-1980 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $p$ | $q$ | $P$ [b] | $Z^L$ [b] | $Z^V$ [b] | $P$ [b] | $Z^L$ [b] | $Z^V$ [b] | $P$ [b] | $Z^L$ [b] | $Z^V$ [b] | $P$ [b] | $Z^L$ [b] | $Z^V$ [b] |
| Benzene [14] | 0.308976 | 0.768571 | 1.07 | 4.34 | 4.95 | 2.83 | 4.43 | 4.95 | 1.13 | 10.14 | 6.25 | 0.44 | 10.14 | 6.25 |
| Isobutane [15] | 0.279677 | 0.871241 | 0.73 | 8.50 | 2.74 | 0.72 | 10.66 | 3.37 | 0.96 | 17.65 | 5.54 | 0.15 | 20.26 | 7.80 |
| *n*-Butane [15] | 0.289844 | 0.870674 | 0.69 | 10.08 | 3.58 | 0.96 | 12.76 | 4.22 | 0.92 | 19.74 | 4.93 | 0.23 | 22.85 | 7.52 |
| Tertiary butanol [16] | 0.451006 | 0.907279 | 1.31 | 4.67 | 5.50 | 15.10 | 6.17 | 5.28 | 1.40 | 9.42 | 7.82 | 0.83 | 10.14 | 8.55 |
| Carbon disulphide [17] | 0.281840 | 0.728321 | 2.27 | 7.21 | 5.76 | 3.36 | 7.34 | 6.73 | 2.65 | 6.78 | 7.08 | 0.59 | 8.30 | 8.03 |
| Deuterium [18] | 0.064150 | 0.615933 | 1.35 | 16.00 | 5.25 | 6.44 | 16.03 | 5.35 | 1.84 | 6.53 | 7.56 | 0.15 | 6.95 | 8.17 |
| Ethane [19] | 0.251832 | 0.837427 | 0.79 | 7.26 | 4.98 | 0.42 | 10.15 | 3.80 | 1.07 | 14.78 | 5.55 | 0.23 | 18.11 | 6.71 |
| Ethyl alcohol [14] | 0.486284 | 0.784743 | 3.82 | 6.03 | 7.50 | 56.64 | 5.40 | 7.46 | 3.87 | 17.83 | 8.97 | 0.19 | 17.83 | 8.97 |
| Hexane [20] | 0.311217 | 0.829202 | 0.59 | 3.65 | 5.58 | 6.25 | 3.75 | 5.56 | 0.68 | 13.76 | 7.14 | 0.38 | 13.82 | 7.15 |
| Hydrogen sulphide [2] | 0.277370 | 0.802614 | 1.07 | 6.97 | 2.54 | 1.00 | 7.02 | 2.53 | 1.25 | 6.17 | 3.58 | 0.12 | 6.26 | 3.59 |
| Methyl alcohol [14] | 0.475962 | 0.748471 | 2.74 | 21.23 | 11.92 | 45.81 | 19.83 | 11.87 | 2.81 | 36.31 | 13.56 | 0.95 | 36.32 | 13.56 |
| Neon [21] | 0.144609 | 0.763227 | 0.73 | 12.51 | 2.20 | 7.85 | 13.13 | 2.01 | 1.02 | 4.71 | 2.81 | 0.30 | 5.42 | 2.91 |
| Isopentane [22] | 0.293960 | 0.860859 | 0.50 | 10.27 | 3.86 | 2.25 | 13.45 | 4.60 | 0.71 | 19.62 | 6.62 | 0.42 | 23.35 | 8.92 |
| Neopentane [23] | 0.277125 | 0.868972 | 0.55 | 8.71 | 4.58 | 1.94 | 10.78 | 3.50 | 0.76 | 17.16 | 5.10 | 0.26 | 19.90 | 5.75 |
| *n*-Pentane [24] | 0.303953 | 0.864676 | 0.77 | 11.56 | 4.61 | 2.84 | 14.30 | 5.02 | 0.78 | 21.43 | 6.76 | 0.16 | 24.74 | 8.73 |
| Water [25] | 0.444423 | 0.734924 | 5.72 | 22.55 | 6.28 | 21.16 | 23.97 | 7.12 | 6.13 | 37.70 | 8.36 | 0.55 | 39.73 | 9.65 |
| Xenon [26] | 0.200003 | 0.794408 | 0.67 | 7.97 | 3.23 | 1.39 | 7.87 | 3.12 | 0.92 | 6.40 | 4.42 | 0.35 | 6.78 | 4.43 |
| RMS% | – | – | 1.49 | 9.97 | 5.00 | 10.40 | 11.00 | 5.09 | 1.70 | 15.65 | 6.59 | 0.48 | 17.11 | 7.45 |

[a] Critical properties, when not available in original sources, have been taken from ref. 2.

[b] RMS% error values.

and $q$, calculated from the saturated liquid–vapour equilibrium data. If required experimental data are not readily available, it may be useful to express the $\alpha(T^*)$ function constants $p$ and $q$ through the Pitzer acentric factor $\omega$. Short calculation shows that the $q$ parameter is weakly dependent on $\omega$ and may be approximated at a constant value of 0.8. The parameter $p$, on the other hand, can be correlated to $\omega$ (data taken from Reid et al. [12]) as:

$$p = 0.1774 + 0.7314\omega - 0.4045\omega^2 \tag{19}$$

For the given compound set (Table 1), eqn. (19) has a correlation coefficient of $\rho^2 = 0.890$.

Table 1 presents, in terms of RMS% errors, a comparison between the results obtained from this work and those calculated by the original Peng–Robinson [1] equation, the Lielmezs et al. [4] modification of the Redlich–Kwong equation and the modification of the Redlich–Kwong equation by Soave [13].

Table 1 indicates that the proposed modification is significantly better than the original Peng–Robinson equation for calculating saturated state vapour pressures. However, it is only slightly better for calculating saturated liquid compressibility factors. Although this work shows marginally smaller errors, there is little significant difference between the two methods in the accuracy of calculated saturated vapour compressibilities.

When the results of the four methods considered here are compared (Table 1), this work gives most accurate results for saturated liquid compressibilities; Peng–Robinson is the second best, Lielmezs et al. [4] and Soave [13] follow. For saturated vapour pressure the Soave equation gives the lowest errors for all compounds, this work shows to be the second best, while the Lielmezs et al. [4] and the original Peng–Robinson equations follow. For saturated vapour compressibilities, the results of this work are not significantly better than those of the Peng–Robinson method. Again, the Lielmezs et al. method is third and Soave is fourth.

Following the calculation procedures already established by Lielmezs et al. [4], the proposed modification of the Peng–Robinson equation (this work) satisfies the following conditions:

(a) It has two adjustable, substance-dependent parameters $p$ and $q$, of which $p$ can be expressed as a non-linear relation of the Pitzer acentric factor, $\omega$ (eqn. 19). Presently, it is suggested that $p$ and $q$ values can be determined from the available saturated liquid–vapour equilibrium data. The required normal boiling point temperatures are usually available.

(b) Although the new attractive force, $\alpha(T^*)$, function in eqns. (13), (14) and (15) is temperature dependent, it becomes unity at the critical state, i.e.:

$$\alpha(T^*) \to 1.0 \qquad T \to T_C \tag{20}$$

and the proposed modification of the Peng–Robinson equation satisfies the necessary conditions at the critical point.

## ACKNOWLEDGEMENT

The financial assistance of the Natural Science and Engineering Research Council of Canada is gratefully acknowledged. The assistance of Ms. H. Aleman with some of the calculations is appreciated.

## NOMENCLATURE

| | |
|---|---|
| $a$, $b$ | coefficients defined by eqns. (2) and (3) as a function of critical temperature and pressure |
| $a(T)$ | temperature-dependent parameter defined by eqns. (5) and (13) |
| $a(T_C)$ | coefficient defined by critical temperature, eqn. (2) |
| $A$, $B$ | dimensionless parameters introduced by eqns. (8) and (9) |
| $f$ | fugacity |
| $N$ | number of data points |
| $p$, $q$ | coefficients defined by eqn. (15) |
| $P$ | pressure |
| $R$ | universal gas constant |
| $T$ | absolute temperature (K) |
| $T^*$ | dimensionless temperature defined by eqn. (14) |
| $V$ | volume |
| $Z$ | compressibility factor |

### *Subscripts*

| | |
|---|---|
| C | critical state |
| r | reduced |
| s | saturated |
| NB | normal boiling |

### *Superscripts*

| | |
|---|---|
| L | liquid state |
| V | vapour state |

### *Greek letters*

| | |
|---|---|
| $\alpha(T^*)$ | dimensionless temperature term dependent on $T^*$, defined by eqns. (14) and (15) |
| $\rho$ | correlation coefficient |
| $\omega$ | Pitzer's acentric factor |

## REFERENCES

1 D.Y. Peng and D.B. Robinson, Ind. Eng. Chem., Fundam., 15 (1979) 59.
2 O. Redlich and J.N.S. Kwong, Chem. Rev., 44 (1949) 233.
3 K.C. Chao and L.R. Robinson (Eds.), Equations of State in Engineering and Research, Adv. in Chem., No. 182, American Chemical Society, Washington, DC, 1979.
4 J. Lielmezs, S.K. Howell and H.D. Campbell, Chem. Eng. Sci., 38 (1983) 1293.
5 R.B. Griffiths, Phys. Rev., 158 (1967) 176.
6 L.P. Kadanoff, Physics, 2 (1966) 263.
7 F. Wegner, Phys. Rev., 35 (1972) 4529.
8 K.G. Wilson and J. Kogut, Phys. Rep., 12C (1974) 75.
9 J. Lielmezs, K.G. Astley and J.A. McEvoy, Thermochim. Acta, 52 (1982) 9.
10 D. Santrach and J. Lielmezs, Ind. Eng. Chem., Fundam., 17 (1978) 93.
11 L.W. Fish and J. Lielmezs, Ind. Eng. Chem., Fundam., 14 (1975) 248.
12 R.C. Reid, J.M. Prausnitz and T.K. Sherwood, The Properties of Gases and Liquids, McGraw-Hill, New York, 1977.
13 G. Soave, Chem. Eng. Sci., 35 (1980) 1725.
14 E.F. Fiock, D.C. Ginnings and W.B. Holton, NBS J. Res., 6 (1931) 881.
15 T.R. Das, C.O. Reed, Jr. and P.T. Eubank, J. Chem. Eng. Data, 18 (1973) 253.
16 L.H. Crone, Jr. and R.C. Johnson, AIChE J., 2 (1956) 252.
17 L.J. O'Brien and W.J. Alford, Ind. Eng. Chem., 43 (1951) 506.
18 H.M. Roder, G.E. Childs, R.D. McCarty and P.E. Anderhofer, Natl. Bur. Stand. (U.S.), Tech. Note, 641 (1973).
19 P.T. Eubank, Adv. Cryog. Eng., 17 (1971) 270.
20 J. Huisman and B.H. Sage, J. Chem. Eng. Data, 9 (1964) 223.
21 R.D. McCarty, R.B. Stewart and K.D. Timmerhaus, Adv. Cryog. Eng., 8 (1963) 135.
22 T.R. Das, C.O. Reed, Jr. and P.T. Eubank, J. Chem. Eng. Data, 22 (1977) 9.
23 T.R. Das, C.O. Reed, Jr., and P.T. Eubank, J. Chem. Eng. Data, 22 (1977) 16.
24 T.R. Das, C.O. Reed, Jr. and P.T. Eubank, J. Chem. Eng. Data, 22 (1977) 3.
25 ASME Steam Tables, C.E. Power Systems, Windsor, CT, 1967.
26 W.B. Streett, L.S. Sagan and L.A.K. Staveley, J. Chem. Thermodyn., 5 (1973) 633.