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# USE OF *F*-FUNCTION IN VAN DER WAALS-TYPE TWO-CONSTANT CUBIC EQUATION OF STATE

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## ABSTRACT

The recently proposed *F*-function of Shaw and Lielmezs, modified to be optimum in the variance four-term polynomial expansion

$$F = \sum_{n=1}^{4} C_n T_r^{(1-n)/2}$$

has been incorporated into the generalized van der Waals-type two-constant equation of state. Expressions for the generalized fugacity coefficient and enthalpy and entropy departure functions have been obtained. The applicability of these functions has been tested by comparing the values of saturated state vapour pressure, liquid and vapour volumes, heat of vaporization, entropy of vaporization and the liquid state internal energy as calculated by means of a Redlich–Kwong and Peng–Robinson form of the generalized cubic equation of state.

## INTRODUCTION

Schmidt and Wenzel [1] have proposed that the van der Waals two-constant cubic equation of state may have the following generalized form

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

where $u$ and $w$ must satisfy the following constraints

$$\begin{aligned} w &> -u-1 \quad \text{for} \quad u \geq -2 \\ w &> u^2/4 \quad \text{for} \quad u \geq -2 \end{aligned} \tag{2}$$

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Shaw and Lielmezs [2] have shown that all Redlich–Kwong-type equations of state of this model may be expressed through their $F$-function as

$$P = \frac{RT}{V-b} - \frac{\Omega_a}{\Omega_b}\frac{RTb}{V(V+b)}F(\omega,\ T_r) \tag{3}$$

where the $F$-function, $F(\omega,\ T_r)$, is given as

$$F = \sum_{n=0}^{m} a_n(\omega) b_n(T_r) T_r^{-n/2} \tag{4}$$

By combining the suggestions of Schmidt and Wenzel [1] and Shaw and Lielmezs [2], and introducing an empirical substance-dependent coefficient set $C_n$ for the product of parameters $a_n(\omega)$ and $b_n(T_r)$ in eqn. (4) the generalized form of the cubic equation of state (eqn. (1)) can be written as

$$P = \frac{RT}{V-b} - \frac{\Omega_a}{\Omega_b}\frac{RTb}{V^2 + ubV + wb^2}F(T_r) \tag{5}$$

where a simplified $F$-function $F(T_r)$ is given as

$$F = \sum_{n=1}^{m} C_n T_r^{(1-n)/2} \tag{6}$$

The optimal number $m$ of coefficients $C_n$ of the simplified $F$-function (eqn.

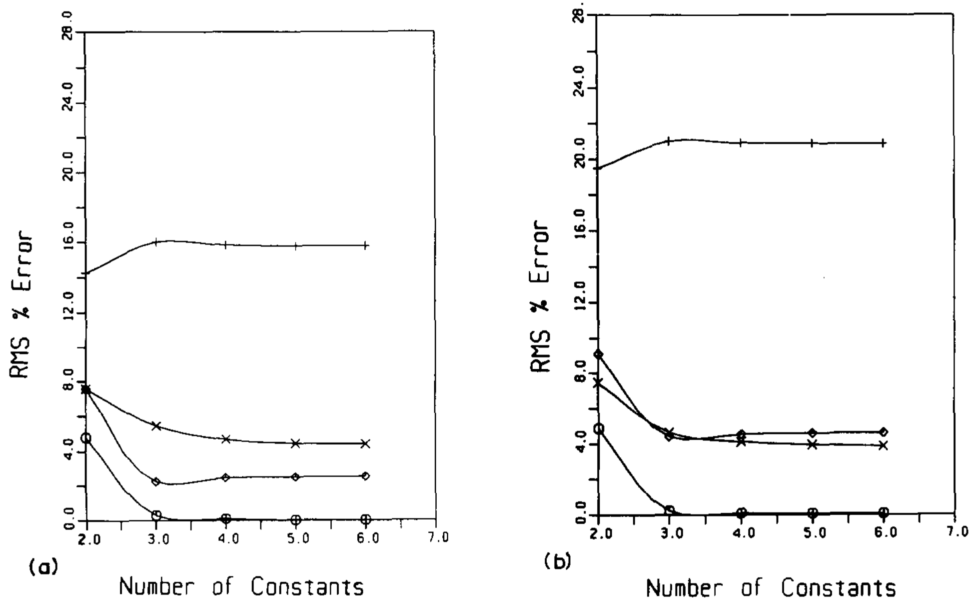

Fig. 1. RMS percentage errors vs. number of RK-type $F$-function constants for (a) ethane and (b) pentane: o——o pressure, $P$; +——+ liquid volume, $V^L$; ◇——◇ vapor volume, $V^V$; ×——× residual liquid internal energy, $U_r^L/RT$.

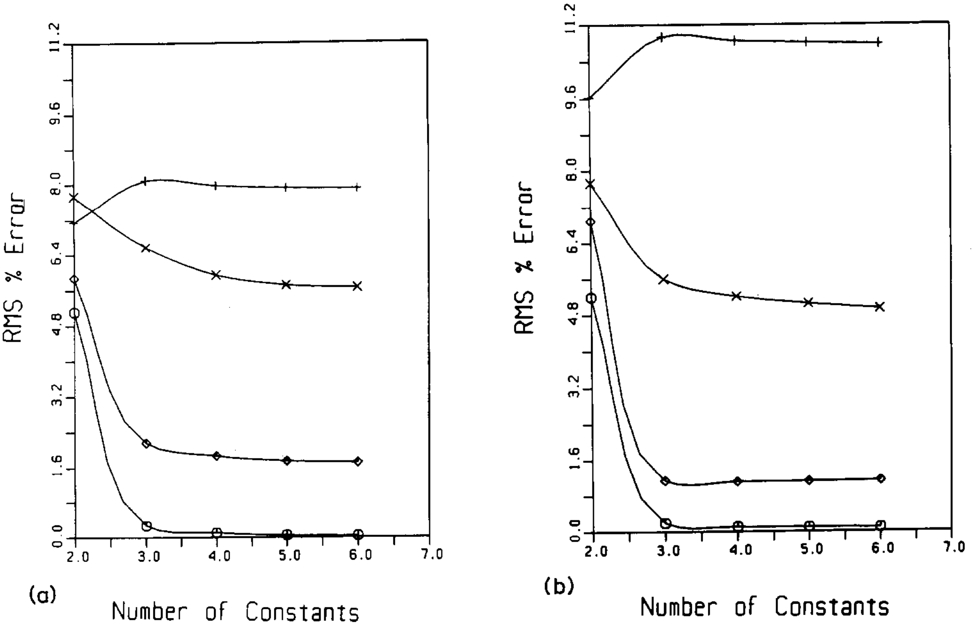

Fig. 2. RMS percentage errors vs. number of PR-type $F$-function constants for (a) ethane and (b) pentane: o——o pressure, $P$; +——+ liquid volume, $V^L$; ◇——◇ vapor volume, $V^V$; ×——× residual liquid internal energy, $U_r^L/RT$.

(6)), when minimized with respect to the RMS percentage error for vapour pressure, liquid and vapour volumes and liquid residual internal energy values (Figs. 1 and 2), was found to be 4, i.e. the $F$-function (eqn. (6)) expanded to four terms may be written as

$$F = C_1 + C_2T_r^{-0.5} + C_3T_r^{-1.0} + C_4T_r^{-1.5} \tag{7}$$

The fugacity coefficient, enthalpy and entropy departure function equations

TABLE 1

Summary of data used

| Compound | Vapour pressure data | | | Physical properties [a] | | | |
|---|---|---|---|---|---|---|---|
| | $T_r$ range | Number of data points | Reference | Critical State | | Normal boiling point, $T_b$ (K) | Pitzer accentric factor |
| | | | | $P_c$ (atm) | $T_c$ (K) | | |
| Ethane | 0.622–0.995 | 18 | [7,8] | 48.20 | 305.42 | 184.47 | 0.098 |
| n-Butane | 0.659–0.997 | 21 | [8,9] | 37.47 | 425.16 | 272.67 | 0.193 |
| iso-Butane | 0.662–0.995 | 19 | [8,10] | 36.00 | 408.13 | 261.32 | 0.176 |
| n-Pentane | 0.660–0.996 | 20 | [8,11] | 33.25 | 469.65 | 309.19 | 0.251 |
| iso-Pentane | 0.673–0.990 | 17 | [8,12] | 33.37 | 460.39 | 301.03 | 0.227 |
| neo-Pentane | 0.669–0.996 | 17 | [8,13] | 31.54 | 433.75 | 282.63 | 0.197 |

[a] Physical properties taken from Reid et al. [6].

TABLE 2

Values for dependent constants $C_{n=1\ldots4}$, Eqns. (5) and (7)

| Compound | Type of $F$-function | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Redlich–Kwong ($F_{RK}$) | | | | Peng–Robinson ($F_{PR}$) | | | |
| | $C_1$ | $C_2$ | $C_3$ | $C_4$ | $C_1$ | $C_2$ | $C_3$ | $C_4$ |
| Ethane | −2.8736678 | 6.3308503 | −4.4508436 | 1.9936611 | −2.0144495 | 4.4767531 | −3.0263897 | 1.5640861 |
| n-Butane | −3.1627778 | 7.0492286 | −5.3222889 | 2.4358382 | −2.1425284 | 4.7800730 | −3.5245281 | 1.8869835 |
| iso-Butane | −2.5922151 | 5.5431311 | −3.9546684 | 2.0037525 | −1.6405889 | 3.4544403 | −2.3176019 | 1.5037506 |
| n-Pentane | −2.8858381 | 6.1029838 | −4.4379360 | 2.2207903 | −1.7673137 | 3.5892880 | −2.4300954 | 1.6081210 |
| iso-Pentane | −7.3944478 | 18.521810 | −15.738836 | 5.6114744 | −5.9644385 | 15.145872 | −12.942339 | 4.7609061 |
| neo-Pentane | −4.8597159 | 11.760073 | −9.6605908 | 3.7602339 | −3.6945721 | 9.0900427 | −7.4947673 | 3.0992968 |

TABLE 3

Comparison of prediction errors

| Compound | RMS percentage error | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $P$ | | | | $V^{L}$ | | | | $V^{V}$ | | | | $U_r^2/RT$ | |
| | SRK [3] | PR [4] | This work | | SRK [3] | PR [4] | This work | | SRK [3] | PR [4] | This work | | This work | |
| | | | $F_{RK}$ | $F_{PR}$ | | | $F_{RK}$ | $F_{PR}$ | | | $F_{RK}$ | $F_{PR}$ | $F_{RK}$ | $F_{PR}$ |
| Ethane | 0.920 | 0.420 | 0.091 | 0.105 | 18.0 | 9.3 | 15.8 | 7.9 | 3.2 | 2.4 | 2.4 | 1.9 | 4.7 | 5.9 |
| n-Butane | 1.115 | 0.769 | 0.095 | 0.116 | 22.6 | 11.9 | 19.3 | 9.8 | 4.9 | 2.3 | 4.0 | 1.6 | 6.9 | 9.7 |
| iso-Butane | 1.036 | 0.700 | 0.042 | 0.057 | 20.7 | 10.6 | 17.2 | 8.5 | 6.2 | 1.5 | 5.3 | 1.3 | 5.1 | 6.3 |
| n-Pentane | 0.991 | 0.336 | 0.096 | 0.109 | 24.3 | 13.4 | 20.9 | 10.8 | 4.8 | 1.0 | 4.6 | 1.1 | 4.1 | 5.2 |
| iso-Pentane | 0.987 | 0.493 | 0.134 | 0.145 | 22.9 | 12.6 | 17.3 | 8.4 | 5.9 | 1.1 | 4.7 | 1.4 | 2.8 | 3.8 |
| neo-Pentane | 0.687 | 0.358 | 0.071 | 0.081 | 20.6 | 10.9 | 17.1 | 8.8 | 3.7 | 2.2 | 2.8 | 1.7 | 4.4 | 5.4 |
| *Average* | 0.956 | 0.513 | 0.088 | 0.102 | 21.5 | 11.5 | 17.9 | 9.0 | 4.8 | 1.8 | 4.0 | 1.5 | 5.0 | 6.1 |

| Compound | Average absolute deviation | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | $H_V$(cal gmol$^{-1}$) | | | | $S_V$(cal gmol$^{-1}$ K$^{-1}$) | | | |
| | SRK [3] | PR [4] | This work | | SRK [3] | PR [4] | This work | |
| | | | $F_{RK}$ | $F_{PR}$ | | | $F_{RK}$ | $F_{PR}$ |
| Ethane | 97.1 | 82.1 | 53.4 | 58.0 | 0.356 | 0.283 | 0.196 | 0.207 |
| n-Butane | 129.7 | 131.7 | 66.2 | 87.2 | 0.321 | 0.330 | 0.170 | 0.223 |
| iso-Butane | 69.0 | 63.7 | 35.7 | 30.4 | 0.181 | 0.167 | 0.101 | 0.082 |
| n-Pentane | 167.3 | 139.8 | 101.2 | 98.2 | 0.406 | 0.327 | 0.253 | 0.240 |
| iso-Pentane | 141.6 | 124.3 | 72.5 | 59.4 | 0.337 | 0.289 | 0.189 | 0.152 |
| neo-Pentane | 164.0 | 142.4 | 101.9 | 102.1 | 0.415 | 0.348 | 0.269 | 0.264 |
| *Average* | 128.1 | 114.0 | 71.8 | 72.6 | 0.336 | 0.291 | 0.196 | 0.195 |

obtained from the generalized cubic equation of state with the simplified *F*-function (eqns. (5) and (6)) are given in the Appendix. The applicability of this set of equations was tested by comparing the values of saturated state vapour pressure, liquid and vapour volumes, heat and entropy of vaporization and the liquid state internal energy as calculated by means of the *F*-function of Redlich–Kwong [3] and Peng–Robinson [4] types of the generalized cubic equation of state [1] obtained by setting $u = 1$, $w = 0$, $u = 2$ and $w = -1$ in eqn. (5), respectively (Appendix, Tables 1–3).

## RESULTS AND DISCUSSION

To study the use of the *F*-function in the van der Waals-type two-constant cubic equation of state (eqns. (1) and (5)) the proposed *F*-function (eqn. (6)) was curve-fitted with saturated vapour pressure data (Table 1). This curve fit was subject to two restricting conditions: first, equality of vapour and liquid state fugacities; and second, noting that at the critical point of vapour–liquid equilibrium the *F*-function becomes unity, that the sum of all *F*-function constants (eqn. (6)) determining the calculated curve fit be 1, or $\Sigma C_n = 1$. The solution of this doubly constrained curve-fitting problem was obtained by means of Lagrange undetermined multipliers which provided the optimum values for the constants $C_n$ (eqn. (6)) for the particular data set.

To establish the number of constants needed to adequately describe the curve fit (eqns. (6) and (7)), the RMS percentage error for saturated state vapour pressure, liquid and vapour volumes and saturated liquid residual internal energy were calculated for the following six hydrocarbons: ethane, n-butane, isobutane, n-pentane, isopentane and neopentane (Table 3). Figures 1 and 2 show the RMS percentage error for vapour pressure, liquid and vapour volumes and liquid residual internal energy plotted against the number of constants for the Redlich–Kwong and Peng–Robinson-type *F*-function for ethane and pentane, respectively. For these compounds (Figs. 1 and 2), as well as for all the other hydrocarbons investigated, the optimum number of curve-fit constants ($C_n$ in eqn. (6)) is four (eqn. (7)). This means that for the hydrocarbon systems considered, an increase in dependence beyond $T_r^{-1.5}$ (eqns. (6) and (7)) does not greatly change the numerical values of properties calculated from a cubic equation (eqn. (5)). Whether this observation can be extended to include hydrogen-bonded and other types of strongly interacting substances, is a matter for further study. Table 2 lists the calculated values of the four substance-dependent constants $C_n$ for the Redlich–Kwong and Peng–Robinson-type *F*-function of the generalized cubic equation of state (eqns. (5) and (6)). Table 3 presents the RMS percentage error values of vapour pressure, saturated liquid and vapour volumes, and enthalpy and entropy of vaporization obtained by means of the generalized four-constants (eqn. (7)) $F$-function for Redlich–Kwong ($F_{\mathrm{RK}}$) and Peng–Robinson ($F_{\mathrm{PR}}$) types, and compares them with results obtained using the Soave–Redlich–Kwong (SRK) and Peng–Robinson (PR) equations of state. It is seen that the four-constant $F$-function (both forms, $F_{\mathrm{RK}}$ and $F_{\mathrm{PR}}$) equation (eqns. (5)–(7)) gives consistently improved predictions over the SRK [3] and PR [4] equations of state in all properties for all substances except saturated vapour volume, where the PR equation of state seems to have a slight edge over the generalized $F_{\mathrm{PR}}$-function.

To compare the RK and PR types in $F$-function cubic equations of state (eqns. (5)–(7); Tables 2 and 3; Appendix) we rewrite the generalized cubic equation of state explicit in pressure (eqn. (1)) as the sum of the repulsion pressure $P_{\mathrm{R}}$ and the attraction pressure $P_{\mathrm{A}}$

$$P = P_{\mathrm{R}} + P_{\mathrm{A}} = \frac{RT}{V-b} - \frac{a}{V^2 + ubV + wb^2} \tag{8}$$

It follows from eqn. (8) that we can write the repulsion pressure $P_{\mathrm{R}}$ term as follows for both the RK and PR types

$$P_{\mathrm{R}} = \frac{RT}{V-b} \tag{9}$$

and the attraction pressure $P_{\mathrm{A}}$ as

$$P_{\mathrm{A}} = \frac{a}{g(V)} \tag{10}$$

where the $g(V)$-function represents the generalized quadratic in volume (eqns. (1) and (8))

$$g(V) = V^2 + ubV + wb^2 \tag{11}$$

Since the RK and PR equations were derived from the same general equation of state (eqn. (5)) in the same way, the only difference between these two forms is the $g(V)$-function as specified by the respective values of constants $u$ and $w$ (eqns. (1), (2), (10) and (11)). Table 3 compares the results obtained by means of the generalized equation of state. One sees that upon changing the $u$ and $w$ values of the $g(V)$-function in eqn. (5), i.e. introducing the RK and PR types of the generalized state equation, the liquid and vapour volume RMS percentage errors of the PR type decrease to half those of the RK form while the derivative properties are not greatly affected. It appears that the accuracy of the derivative properties depends more on the accuracy of the vapour pressure data than on the vapour or liquid volumes. Recently, Yu et al. [5] have shown that there might be a family of $u$ and $w$ values which give a balanced representation of the volumetric properties in different regions of the $P$–$V$–$T$ surfaces.

Comparing the results given in Table 3, we may draw the following conclusions.

(a) The use of four coefficients in the proposed method for vapour pressure prediction increases the accuracy for vapour volume, enthalpy and entropy of vaporization, and liquid residual internal energy but decreases the predictive accuracy for liquid volumes by 1 to 2 RMS %.

(b) The predictive accuracy for liquid and vapour volumes seems to depend on the $g(V)$-function of the attraction pressure term. Whether there is a $g(V)$-function which may minimize the predictive error in volumetric calculation, is an open question.

(c) Most cubic equations for which the attractive force constant $a$ is expressed as a function of temperature can be written in the form of eqn. (5).

(d) The optimal number of constants in the $F$-function is 4 as represented by eqn. (7). Whether this is true for strongly interacting compounds is a subject worthy of further study.

## APPENDIX

The generalized cubic equation of state

$$P = \frac{RT}{V-b} - \frac{\Omega_a}{\Omega_b} \frac{RTb}{V^2 + ubV + wb^2} F$$

in terms of compressibility factor is

$$Z^3 + (uB - B - 1)Z^2 + (A + wB^2 - uB - uB^2)Z - (AB + wB^2 + wB^3) = 0$$

where

$$A = \Omega_a \frac{P_r}{T_r} F$$

$$B = \Omega_b \frac{P_r}{T_r}$$

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

$$F = \sum C_n T_r^{(1-n)/2}$$

The fugacity coefficient is given by the equation

$$\ln\left(\frac{f}{P}\right) = (Z-1) - \ln(Z-B) + F\Phi_1 \ln\left(\frac{Z+\theta_2 B}{Z+\theta_3 B}\right)$$

where

$$\Phi_1 = \frac{\Omega_a}{2\Omega_b\theta_1}$$

$$\theta_1 = \left(u^2/4 - w\right)^{0.5}$$

$$\theta_2 = \frac{u}{2} + \theta_1$$

$$\theta_3 = \frac{u}{2} + \theta_1$$

The enthalpy departure function is written as

$$S - S^0 = R\ \ln(Z - B) + R\ \ln\left(\frac{P_0}{P}\right) + \Phi_1\Phi_2\ \ln\left(\frac{Z + \theta_2 B}{Z + \theta_3 B}\right)$$

where

$$\Phi_2 = -R\left(F + T_r\frac{\mathrm{d}F}{\mathrm{d}T_r}\right)$$

$$P_0 = 1\ \text{atm}$$

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