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GENERALIZED LIQUID VOLUME SHIFTS FOR THE PENG-ROBINSON EQUATION OF STATE FOR C_1 TO C_8 HYDROCARBONS

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***Abstract* — A new generalized correction equation for specific volume of liquid hydrocarbons is proposed. The equation can be used with the Peng-Robinson equation of state (PR) in a wide temperature range and does not require additional parameters for each substance. The equation has been developed for normal hydrocarbons from methane to octane and the obtained results when it is applied to other substances are analyzed. A comparison is also made with the equation proposed by Peneloux *et al.* (1982) resulting, in all cases, in a better performance of the equation proposed here.**

***Keywords* — Specific volume, Liquid hydrocarbons, Peng-Robinson equation of state.**

I. INTRODUCTION

The first equations widely accepted for calculations of liquid specific volumes (or densities) were, apparently, the modified Rackett equation (Spencer and Danner, 1972) and the COSTALD model (Hankinson and Thomson, 1979), which can be used to predict liquid densities within approximately 1% of deviation (% dev = $(v^{calc}-v^{exp})*100/v^{exp}$). However, they are typically applicable only in the subcritical range and as a result, there is a discontinuity in specific volume calculations when moving from saturated to dense liquid.

Later, Peneloux *et al.* (1982) proposed a constant volume correction (known as "specific volume shift") for the Soave-Redlich-Kwong (SRK) cubic equation of state (EOS) (Soave, 1972). The correction is particular for each substance and it is independent of temperature. In the paper, the authors try to generalize the constants used in the correction equation through the Rackett compressibility factor, Z_{RA}.

The procedure works reasonably well for hydrocarbons (with deviations below 5%) when the temperature is far from the critical point. The method fails for reduced temperatures higher than 0.65 (as can be shown below) due to a substantial increment in the specific volume deviations obtained with SRK equation as the temperature increases (Hoyos, 2000).

Watson *et al.* (1986) proposed a correction equation for specific volume of liquids for the Peng-Robinson equation of state (PR) (Peng and Robinson, 1976). The correction is an exponential function of temperature that can be used only in the region close to the critical point.

Although many other equations of volume shift have appeared in the last years (Mathias *et al.*, 1989; Monnery *et al.,* 1998; Sant' Ana *et al.*, 1999), which apparently work reasonably well in the range from triple point to critical point, they require two or three additional parameters for each substance which, in most cases, must be found experimentally and, as a result, this kind of corrections are less attractive for fast calculations.

To avoid all these difficulties, in this paper is proposed a new correction equation to calculate the specific volume of liquid hydrocarbons, which does not require additional parameters for each substance and can be applied in a wide temperature range. Additionally, the results produced when the equation proposed here is applied to other substances like oxygen, nitrogen and water are analyzed.

II. EQUATIONS FOR SPECIFIC VOLUME SHIFT OF LIQUIDS.

The liquid volume shift for the SRK equation proposed by Peneloux *et al.* (1982) is:

$$V_{corr} = V_{SRK} - C_{PEN} \tag{1}$$

Where C_{PEN} is a particular constant for each substance that must be found experimentally but which is generalized as:

$$C_{PEN} = 0.40768(0.29441 - Z_{RA})\frac{RT_c}{P_C} \tag{2}$$

and the Rackett compressibility factor, Z_{RA}, can be calculated as (Reid *et al.*, 1987) :

$$Z_{RA} = 0.29056 - 0.08775\omega \tag{3}$$

The use of Eqs. 1 to 3 produces little improvement when it is compared with the SRK equation, but their results are not better than those obtained with the PR equation, as can be seen in Figs. 1 and 2 where the relative deviations in saturated liquid volume are plotted versus the reduced temperature for methane and ethane, respectively.

As can be seen, constant volume shifts like Eq. 2, does not take into account that the relative deviation obtained with the SRK equation increases with temperature. For the case of normal hydrocarbons considered here (from methane to octane), the correction of Peneloux *et al.* (1982) is not accurate (deviations higher than 5%) for reduced temperatures higher than aprox. 0.65. (Table 1)

Table 1 Temperature ranges where the Peneloux equation produces relative deviations in saturated liquid volume higher than 5%

Substance	T_r
Methane	0.619-1.000
Ethane	0.610-1.000
Propane	0.641-1.000
Butane	0.635-1.000
Pentane	0.636-1.000
Hexane	0.579-0.978
Heptane	0.651-1.000
Octane	0.630-0.960

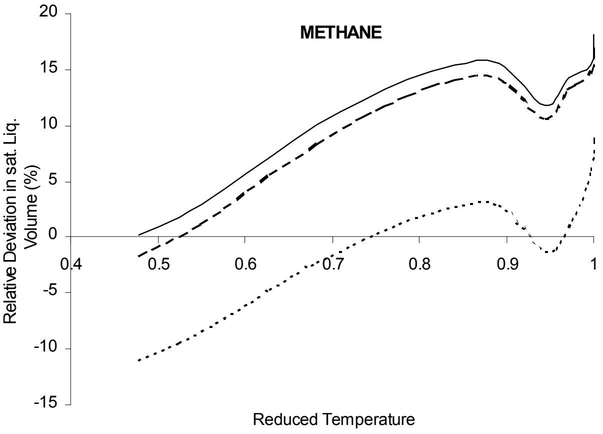

Fig. 1. Relative deviation in saturated liquid volumes for methane calculated with: SRK(___), Peneloux *et al.*, 1982, (- - -) and PR (.....) Eqs.

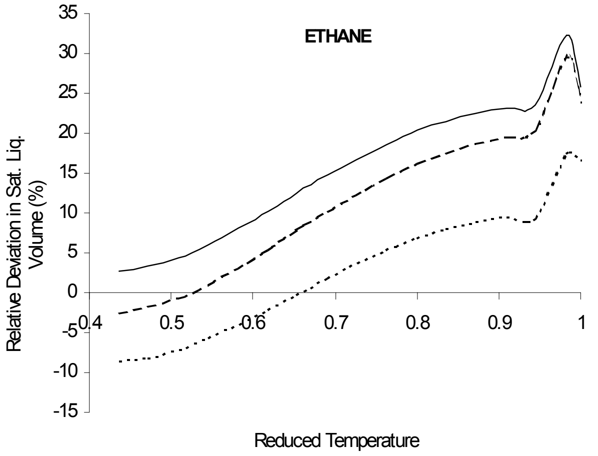

Fig. 2. Relative deviation in saturated liquid volumes for ethane calculated with: SRK(___), Peneloux *et al.*, 1982, (- - -) and PR (.....) Eqs.

Among the great number of volume shifts proposed in literature, the model of Monnery *et al.* (1998) has "has captured some attention. This model is a gaussian-like volume shift for the Peng-Robinson EOS:

$$V_{corr} = V_{PR} + C \tag{4}$$

where V_{PR} is the specific volume calculated with the PR equation and C is defined as:

$$C = C_1 + \frac{C_4}{\sqrt{2\pi C_2}} \exp\left[-0.5 \left(\frac{T_r - C_3}{C_2} \right)^2 \right] \tag{5}$$

With the dimensional constant C_4 set to 1 m^3/kmol and the parameters C_1 to C_3 are specific for each substance.

Even though the low absolute deviations obtained when using Eqs. 4 and 5, the model is not recommended for the dense state at pressures above the critical. Furthermore, it requires three new constants for each substance, which makes it computationally expensive

III. THE NEW VOLUME SHIFT MODEL

In earlier studies (Hoyos, 2000) it was shown that, for liquid volume calculations, the PR equation is superior to EOS like SRK and RK and it has comparable results (and sometimes superior) with EOS of higher complexity as Valderrama-Patel-Teja (Valderrama, 1990) and Carnahan-Starling-Stryjek-Vera (Zabaloy and Vera, 1998). All these results allow the selection of the PR equation as the base line to develop a new model for specific volume correction.

The substances selected for this work were the normal hydrocarbons from methane to octane whose saturated liquid specific volumes were calculated for 30 equally spaced points in the temperature range from the triple point to the critical point of each substance. The PR equation was solved numerically through the Bairstow method, which founds roots sequentially and has high numerical stability (Monton *et al.*, 1986). The PR equation was forced to reproduce exactly the pure compound vapor pressure, at each particular temperature value.

The database selected to relative deviation calculations was taken of Starling (1973). Additionally, Benedict-Webb-Rubin interpolations were performed when necessary.

By inspection of the obtained deviation tendency of calculations with the PR equation and to gain simplicity, in this work the liquid volume was calculated with a correction similar to Eq. 4, but instead of a Gaussian correction, the proposed correction is a parabolic function of temperature:

$$C = C_1 + C_2 (T_r - C_3)^2 \tag{6}$$

where C_3 can be understood as the value of reduced temperature where the maximum correction is required and C_1 as the value of that maximum correction.

The value of C_3 is obtained as the average of reduced temperature where the maximum deviation of the original PR equation for saturated liquid volumes occurs, yielding $C_3 = 0.89$.

On the other hand, at the particular reduced temperature value where the PR equation does not need correction, the Eq. 6 becomes:

$$\frac{C_1}{C_2} = -(T_{r(\%desv=0)} - 0.89)^2 \tag{7}$$

The C_1/C_2 ratio can be calculated as a polynomial function of the acentric factor as shown in Fig. 3. The function obtained (with a correlation coefficient of 0.9971) is:

$$\frac{C_1}{C_2} = 110.07\omega^4 - 83.807\omega^3 + 18.926\omega^2 - 1.6348\omega - 0.0066 \tag{8}$$

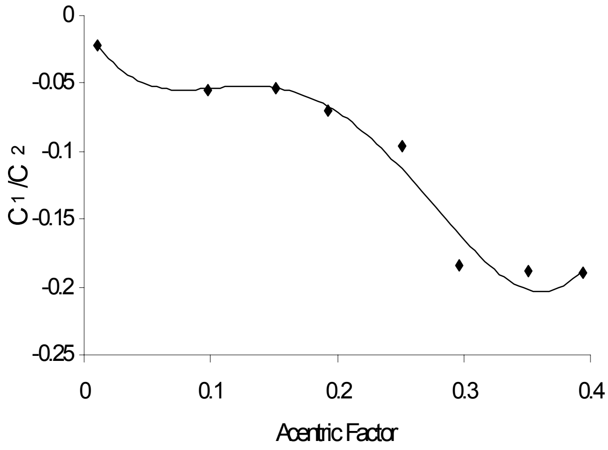

Fig. 3. Variation of C_1/C_2 ratio with acentric factor

The C_2 constant remains as a degree of freedom, which is found as the value that minimizes the average of absolute value of relative deviations for all substances, yielding:

$$C_2 = 2.013645 * 10^{-3}\ m^3/kg \tag{9}$$

With all the considerations stated above, the new equation to calculate the specific volume of liquid C_1 to C_8 hydrocarbons is:

$$V_{corr} = V_{PR} + \left(\frac{C_1}{C_2}\right) C_2 + C_2 (T_r - C_3)^2 \tag{10}$$

Table 2 shows the relative deviations of SRK, PR, Peneloux *et al.* (1982) and the correction proposed here with respect to experimental data. The results of Table 2 are quite illustrative since, as can be seen, the use of Eq. 10 reduces the overall average deviation from 8.94 (obtained with the PR equation) to 3.82% and produces the lowest deviation for the hydrocarbons considered in this study.

Figures 4 to 8 (and Table 2) show the improvement in saturated liquid volume calculations when Eq. 10 is used. The average deviation is lower than 4% for almost all substances, except for heptane (Fig. 7), where the average deviation reaches a value of 8.4 %

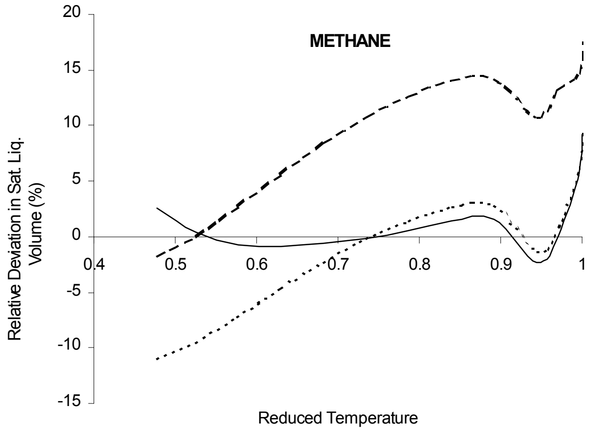

Fig. 4. Relative deviations in saturated liquid volumes for methane calculated with: Eq. 10 (___), Peneloux *et al.*, 1982, (- - -) and PR (.....).

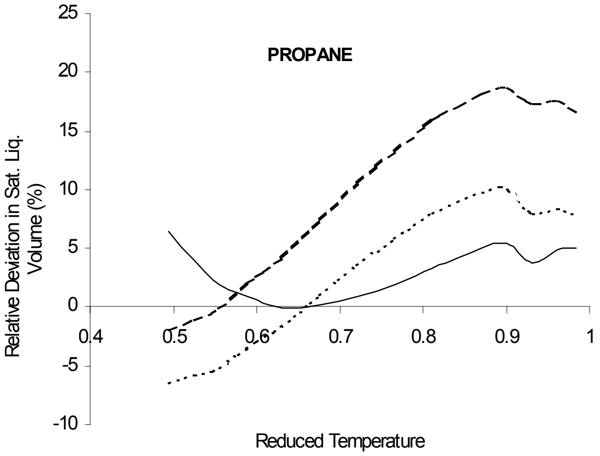

Fig. 5. Relative deviations in saturated liquid volumes for propane calculated with: Eq. 10 (___), Peneloux *et al.*, 1982, (- - -) and PR (.....).

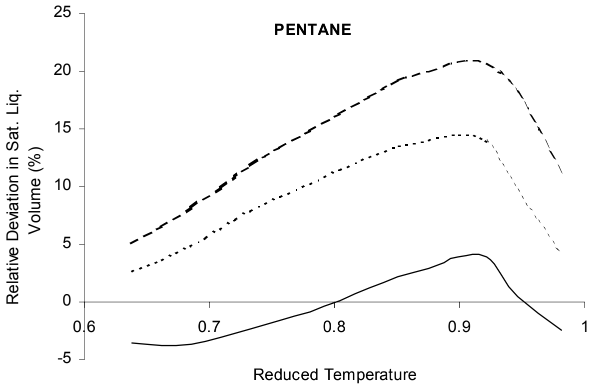

Fig. 6. Relative deviations in saturated liquid volumes for pentane calculated with: Eq. 10 (___), Peneloux *et al.*, 1982, (- - -) and PR (.....).

Table 2. Average and maximum $^{(a)}$ relative deviations (%)$^{(b)}$ in saturated liquid specific volumes obtained with the SRK and PR EOS and their volume shift equations.

Substance	SRK (%)	Peneloux (%)	PR (%)	Eq. 10 (%)
Methane	10.83	9.72	4.59	2.00
	(18.16)	(17.48)	(10.92)	(9.21)
Ethane	16.09	12.66	7.73	3.44
	(32.27)	(29.51)	(17.40)	(14.88)
Propane	16.17	10.84	6.23	3.18
	(23.79)	(18.83)	(10.15)	(6.44)
Butane	21.80	14.86	8.26	3.68
	(29.30)	(23.19)	(15.02)	(8.96)
Pentane	23.02	14.28	9.26	2.39
	(28.80)	(20.89)	(14.57)	(3.92)
Hexane	23.65	12.64	10.65	3.39
	(32.42)	(22.82)	(17.80)	(5.49)
Heptane	25.32	12.26	11.48	8.40
	(35.55)	(27.28)	(21.85)	(12.18)
Octane	26.39	12.01	13.58	4.04
	(38.94)	(25.99)	(23.56)	(7.41)
Overall average	**20.41**	**12.42**	**8.94**	**3.89**

a) Values in parentheses are maximum percent deviations

b) % dev = $|(V_{equation} - V_{database})|*100/V_{database}$

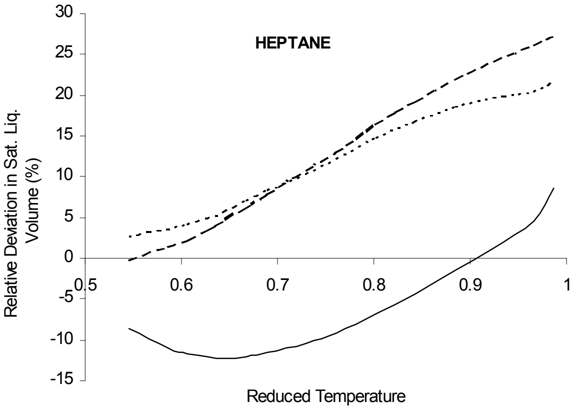

Fig. 7. Relative deviations in saturated liquid volumes for heptane calculated with: Eq. 10 (___), Peneloux *et al.*, 1982, (- - -) and PR (.....).

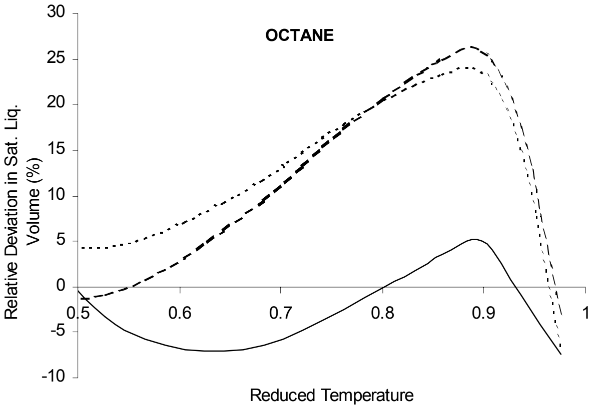

Fig. 8. Relative deviations in saturated liquid volumes for octane calculated with: Eq. 10 (___), Peneloux *et al.*, 1982, (- - -) and PR (.....).

As has been pointed out by Pfohl (1999), introducing a temperature-dependent volume translation into an equation of state can lead to inconsistent description of isotherms. The risk is that the isotherms may cross each other, especially at temperatures near the critical and in the region of high densities.

A way of evaluating whether the new equation is consistent is by computing the partial derivative of pressure with respect to temperature at constant volume. A negative sign for such derivative is indicative (in most cases) of an inconsistent behavior for the model.

Figures 9 and 10 show this evaluation for butane and hexane, respectively, in a range of T_r between 0.6 and 1.2 and reduced pressures upon 10. The lines are constant volume to co volume ratios (co volume = parameter b in PR equation of state). Similar results are obtained for all other substances. As can be seen, the new equation leads to consistent isotherms.

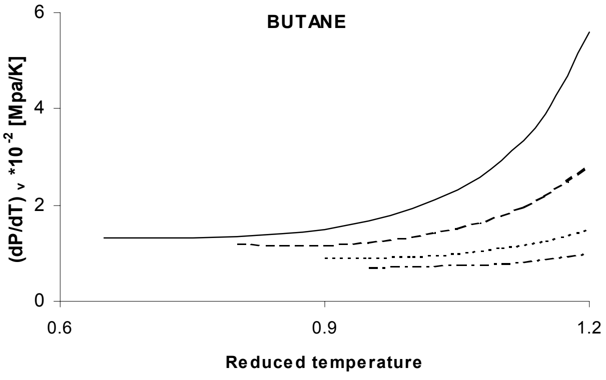

Fig. 9. Evaluation of $\partial P/\partial T)_v$ for butane. The lines are constant volume to co-volume ratios (v_{corr}/b) at 1.0 (upper), 1.5, 1.8 and 2.0 (lower)

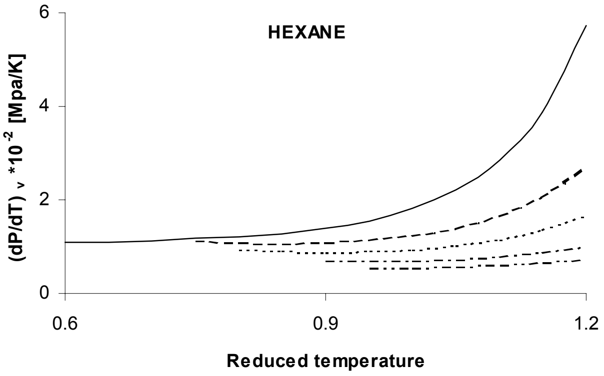

Fig. 10. Evaluation of $\partial P/\partial T)_v$ for hexane. The lines are constant volume to co-volume ratios (v_{corr}/b) at 0.95 (upper), 1.35, 1.50, 1.7 and 1.95 (lower)

IV. APPLICATION TO COMPRESSED LIQUID AND OTHERS SUBSTANCES

To verify the possible application of the volume shift proposed in this study to liquids below their saturation point, the specific volume of hydrocarbons at low temperatures and atmospheric pressure were calculated. Figures 11 and 12 show the relative deviations for ethane and butane. The equation proposed works well for high temperatures but gives higher relative deviations than the original PR equation for lower reduced temperatures (this behavior is typical for all hydrocarbons studied). Table 3 shows the reduced temperatures where the volume shift begins to fail.

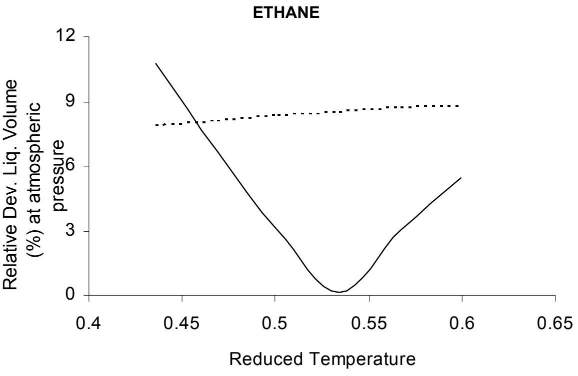

Fig. 11. Relative deviations in liquid volumes of ethane at atmospheric pressure calculated with: Eq. 10 (___) and PR (.....).

Table 3 Reduced temperatures where Eq. 10 gives relative deviations higher than the PR equation

Substance	Tr
Methane	0.48
Ethane	0.46
Propane	0.47
Butane	0.49
Pentane	0.46
Hexane	0.47
Heptane	0.49
Octane	0.44

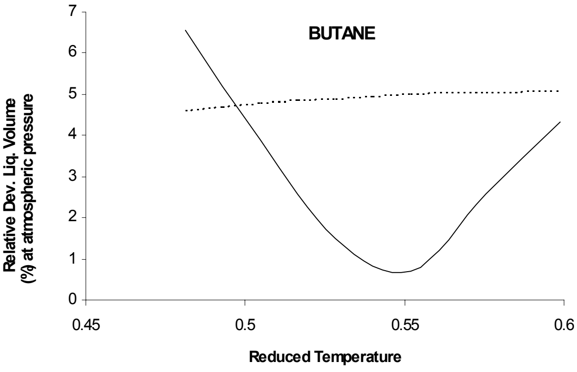

Fig. 12. Relative deviations in liquid volumes of butane at atmospheric pressure calculated with: Eq. 10 (___) and PR (.....).

Additionally, the relative deviations in saturated liquid volume obtained for water, nitrogen and oxygen were analyzed. The procedure for these cases was the same used previously for hydrocarbons.

The results of applying Eq. 10 to saturated liquid volume calculations for water, nitrogen and oxygen are shown in Figs. 13 to 15 and in Table 4. As for the hydrocarbon case, the use of the volume shift proposed here yields the lowest average deviations.

For water, the specific volumes predicted are significantly improved for reduced temperatures higher than 0.45, but unfortunately the relative deviations are still around 10% for reduced temperatures higher than 0.85 (although always the Eq. 10 produces the lowest deviations).

For nitrogen and oxygen, there is little improvement in results and a change in the relative deviations sign when using Eq.10.

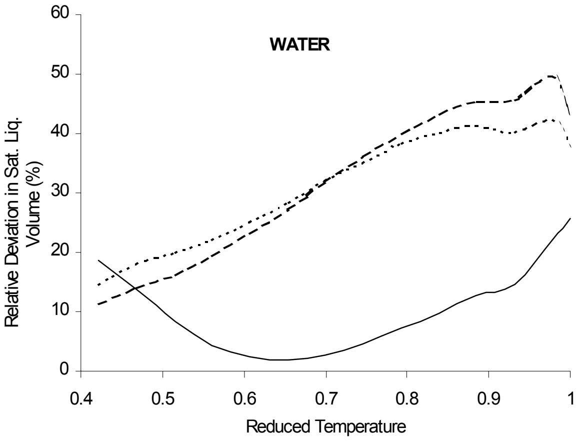

Fig. 13. Relative deviations in saturated liquid volumes for water calculated with: Eq. 10 (___), Peneloux (- - -) and PR (.....).

Table 4. Analyzed temperature range and average and maximum deviations for saturated liquid volumes of water, nitrogen and oxygen

Substance	Range of Tr	SRK (%)	Peneloux (%)	PR (%)	Eq. 10 (%)
Water	0.422-1.000	47.11 (59.59)	31.90 (49.66)	31.14 (32.47)	10.63 (25.78)
Nitrogen	0.500-1.000	12.03 (26.39)	9.95 (24.95)	5.75 (14.02)	4.45 (10.79)
Oxygen	0.615-1.000	13.25 (17.72)	11.66 (16.51)	3.85 (8.53)	3.00 (6.71)

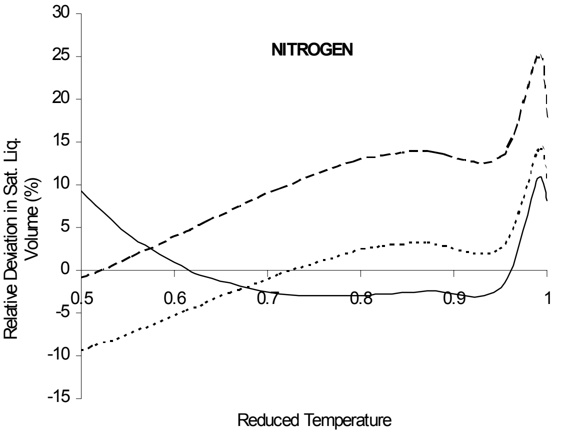

Fig. 14. Relative deviations in saturated liquid volumes for nitrogen calculated with: Eq. 10 (___), Peneloux (- - -) and PR (.....).

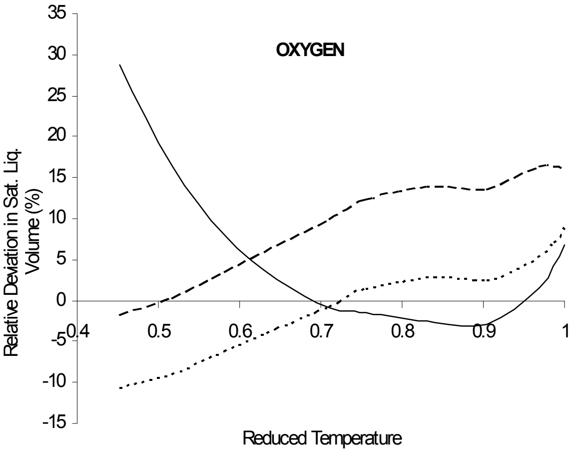

Fig. 15. Relative deviations in saturated liquid volumes for oxygen calculated with: Eq. 10 (___), Peneloux (- - -) and PR (.....).

V. CONCLUSIONS

In this work, it has been shown that a constant specific volume shift like that of Peneloux *et al.* (1982) is not satisfactory for calculations of liquid volumes of hydrocarbons. On the other hand, a more complex correction (like Eq. 5) is not an attractive option for fast engineering calculations.

The liquid volume shift for normal hydrocarbons (methane to octane) proposed here is a generalized temperature function, which does not require additional parameters for each substance and produces lower relative deviations than Peneloux model (should be keep in mind than the results of this work were obtained by fitting the constants to experimental information for eleven compounds, while, on the other hand, for the other three equations of state appearing in Table 2, the databases that the original authors used were wider than the database used here).

The Eq. 10 produces consistent isotherms calculations and becomes an alternative that can be used with confidence in the reduced temperature range between 0.5 and 1.0 for saturated liquid as well as compressed liquid hydrocarbons with deviations lower than 4%.

Additionally, Eq. 10 highly improves the value of liquid volume of water obtained with the Peng-Robinson EOS and can also be used for substances like nitrogen and oxygen

NOMENCLATURE

C	Liquid specific volume shift
C_1,C_2	Correction coefficients of liquid specific volume.
P	Pressure
R	Universal gas constant.
T	Temperature
v	Specific volume.
Z	Compressibility factor
ω	Acentric factor
Subscripts	
C	Critical point
Corr	Corrected value
PEN	Obtained with Peneloux model
PR	Obtained with the Peng-Robinson equation of state
r	Reduced properties
RA	Rackett.
SRK	Obtained with Soave-Redlich-Kwong equation of state
Abbreviations	
EOS	Equations of State
dev.	Deviation
PR	Peng – Robinson
RK	Redlich-Kwong
SRK	Soave – Redlich – Kwong

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