

GENERALIZED LIQUID VOLUME SHIFTS FOR THE PENG-ROBINSON EQUATION OF STATE FOR C₁ TO C₈ HYDROCARBONS

B. HOYOS

*Escuela de Procesos y Energía. Universidad Nacional de Colombia, A. A. 1027. Medellín, Colombia.
bahoyos@unalmed.edu.co*

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 = $(v^{\text{calc}} - v^{\text{exp}}) * 100 / v^{\text{exp}}$). 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:

$$V_{\text{corr}} = V_{\text{SRK}} - C_{\text{PEN}} \quad (1)$$

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

$$C_{\text{PEN}} = 0.40768(0.29441 - Z_{RA}) \frac{RT_c}{P_c} \quad (2)$$

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

$$Z_{RA} = 0.29056 - 0.08775\omega \quad (3)$$

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