



A generalized cubic equation of state for non-polar and polar substances



Luis A. Forero G*, Jorge A. Velásquez J

Pulp and Paper Research Group, Faculty of Chemical Engineering, Universidad Pontificia Bolivariana, Circular 1° # 70-01, Medellín Antioquia, Colombia

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ABSTRACT

A modified version of the Peng–Robinson equation of state (EoS) is developed to describe the thermodynamic properties of polar and non-polar substances. The modified EoS is obtained after replace the alpha function of Soave by the alpha function of Heyen in the pressure–volume–temperature relationship of the Peng–Robinson EoS. The parameters of the EoS are correlated in terms of the critical temperature, the critical pressure, the acentric factor and the polar factor of Halm–Stiel to obtain generalized expressions by fitting two vapor pressure data for 67 polar compounds and 23 n-alkanes.

To validate the EoS, vapor pressures are calculated for 178 polar and 81 non –polar compounds. The average absolute relative deviation calculated is 1.51%. In total, 8440 vapor pressure data are calculated for polar substances and 2281 for gases and hydrocarbons. The modified EoS is compared with a modified Patel–Teja equation that requires substance-dependent parameters, the Peng–Robinson EoS and a generalized version of the Peng–Robinson–Stryjek–Vera EoS. The calculated deviations are 6.17%, 6.68% and 1.27% for the PR, the gPRSV and the PTH EoSs.

Additionally, to improve liquid densities estimations, the modified EoS is translated in volume by fitting one saturated liquid volume. The translation-parameter is generalized for gases and hydrocarbons and it is estimated and reported for 179 polar compounds. Saturated liquid densities are calculated for 259 substances. The calculated average absolute relative deviation is 1.70%. This value is practically the same calculated with the PTH EoS. Also, single-phase density calculations including pressures above 100 MPa are performed for some gases, alkanes and polar substances. It has been found that results are better with the proposed model, especially for heavy hydrocarbons. For example, the deviations for n-tetracosane are 6.2% and 13% for the modified and the PTH EoSs. Similar results are obtained for other compounds like n-eicosane and n-octacosane.

On the other hand, heat capacity at constant pressure for the saturation curve and the single phase region is predicted with the modified, the PR and the PTH EoSs for 20 compounds. Results show that average absolute relative deviations for all the models are similar and their values are around 5.0% for the saturated liquid, 7.0% for saturated vapor and 4.0% for the single phase region. Finally, the modified EoS is used to predict the vapor pressure, the saturated liquid volume and the heat capacity in the single phase region of water. In general, results can be considered adequate taking into account the simplicity of the proposed EoS. Calculated deviations are 0.75%, 4.34% and 5.17% for the three properties selected.

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1. Introduction

Chemical engineers employ equations of state to simulate, evaluate, design and optimize chemical processes. EoSs are considered the cornerstone of thermodynamic models because

they can be used to perform phase equilibria calculations and at the same time they can be employed to calculate thermal and volumetric properties in wide temperature and pressure ranges [1]. Additionally, EoSs can be coupled with different theories to correlate other properties like viscosity or interfacial tension [2–6].

In general, EoSs can be classified as reference, cubic or molecular-based equations. However, engineers normally prefer cubic EoSs because they are simple models that allow fast and reliable calculations for pure substances and mixtures [7,8].

* Corresponding author.

E-mail addresses: luis.foreroga@upb.edu.co (L.A. Forero G), jorge.velasquezj@upb.edu.co (J.A. Velásquez J).

According to literature, parameters of cubic EoSs can be adjusted in different ways to obtain acceptable results for industrial applications [9].

Despite that there are many cubic EoSs available in literature. The Soave-Redlich-Kwong [10] and the Peng–Robinson [11] EoSs are the most popular and the most used thermodynamic models in academia and industry. These two EoSs can predict the vapor pressure of gases, light-medium weight hydrocarbons and non-polar compounds [12]. For another compounds like heavy hydrocarbons, some modified PR EoSs have been developed as generalized models in terms of the acentric factor to improve the capabilities of the original EoS [13–15].

On the other hand, the literature establish that the capability of a cubic EoS to describe the vapor pressure of polar substances is related directly to the alpha function incorporated in the attractive term of the EoS [12]. The alpha function of the original SRK and PR EoSs is that proposed by Soave in 1972. In general, the alpha function of Soave is not adequate to correlate the vapor pressure of polar substances. For this reason, some alpha functions have been developed and coupled to the PR and SRK EoSs to describe polar and non-polar substances simultaneously [16–20].

Although some modified versions of the PR and SRK EoSs can be used to correlate the vapor pressure of any substance, these kind of equations could present three disadvantages:

- i. In first place, the mathematical behavior of the alpha function can be inadequate. The alpha function of Soave and some of its modified versions can pass through a minimum value above the critical temperature for different substances. According to Segura et al., if the minimum exist, a Boyle temperature without physical sense can be predicted [21]. It is also possible that two isotherms can cross each other. This fact, does not satisfy the Gibbs phase rule in the pressure–volume diagram of a pure substance. However, according to Neau et al., for practical purposes the alpha function of Soave can be used in the ranges of temperature and pressure that are normally involved in industrial applications [22,23].
- ii. In second place, the modified SRK and PR EoSs developed for polar compounds are normally substance-dependent. There are some relative extensive databanks for different equations like the modified Peng–Robinson EoSs proposed by Stryjek and Vera [20], by Mathias–Copeman [24], by Melhem–Saini–Goodwin [16,25], by Twu et al. [26] etc. However, if a substance is not reported in a databank, there is not available a generalized and simple EoS that can be used to predict reliably its vapor pressure. This fact is important even for mixtures because good vapor pressures values are necessary to represent the phase equilibria of mixtures adequately [27].
- iii. Finally, the SRK, the PR EoSs and its modified versions can be classified as two parameter cubic EoSs (2P-EoSs). These EoSs are not recommended to perform liquid volumes calculations because a 2P-EoS predict the same critical compressibility factor for all fluids. A better alternative are the so-called three parameter EoS (3P-EoS) [28].

In a 3P-EoS, each substance has its own semi-empirical critical compressibility factor. Normally, this factor has to be different to the recommended critical compressibility factor to obtain good saturated liquid densities at reduced temperatures below 0.9 [29]. There are different 3P-EoSs reported in literature [7,14,30–35]. For these equations, there are necessary the parameters of the alpha function and the semi-empirical critical compressibility factor. All these parameters are estimated by fitting saturated liquid densities

and vapor pressures simultaneously. For this reason, some authors prefer the translation technique in volume proposed by Peneloux et al. [36].

According to literature, applying to a 2P-EoS a temperature-independent translation in volume and fitting a single saturated liquid volume, saturated liquid densities can be represented very well if the reduced temperature value is below 0.8 [37]. Using this technique, the phase equilibria calculations obtained with the non-translated EoS are not altered by the translation [38]. Based on this concept, Gmehling et al., developed a Peng–Robinson translated EoS using the alpha function proposed by Twu et al. The EoS is known in literature as the VTPR model. The VTPR EoS have been used to represent the phase equilibria and thermodynamic properties of different kinds of compounds and mixtures [26,39–41]. For mixtures Gmehling et al. have developed a group contribution method to predict binary interaction parameters [41]. However for pure substances, due to the functionality of the alpha function of Twu et al., the EoS is not generalized and it requires substance-dependent parameters.

In order to solve the three problems described in the paragraphs above, a modified Peng–Robinson EoS is proposed in this work. The new model is based on the Peng–Robinson pressure–volume–temperature relationship and the alpha function developed by Heyen at the ends of the 70's [42].

The selection of the alpha function of Heyen is based on a recent work presented by the authors [43]. In that work, the performance of six alpha functions coupled to the Peng–Robinson and the Patel–Teja EoSs was evaluated. The functions evaluated were those developed by Heyen, Melhem et al., Trebble-Bishnoi, Gasem et al., Haghtalab et al. and Soave respectively. The authors found that the alpha function of Heyen was the best alternative because it can be used to describe correctly the vapor pressure, the saturated vapor volume and the enthalpy of vaporization of non-polar and polar compounds. Also it is an exponential alpha function that is monotonic descendent and does not present the problems described by Segura et al. for the Soave type functions [21]. Finally the alpha function can be generalized in terms of the acentric factor at least for gases and hydrocarbons [43].

To obtain a 2P-EoS valid for polar or non-polar substances, the EoS is generalized in terms of the critical temperature, the critical pressure, the acentric factor and the polar factor of Halm-Stiel [43]. The first three parameters are available for many substances in the databank reported by Poling et al. [44] or by Daubert et al. [45]. However, the information about polar factor is limited and for this reason a simple method to estimate it and a databank is reported in this work. To validate the generalized 2P-EoS, vapor pressures predictions are performed for more than 150 substances.

On the other hand, to improve the capability of the model to describe liquid densities, the proposed EoS is translated in volume using the recommendations of Gmehling et al. [26]. A procedure to estimate the translation parameter from a single liquid density is described and implemented. The translated volume is generalized for gases and hydrocarbons. For polar substances the parameter of translation is reported and added to the databank developed for the polar factor.

To validate the proposed EoS, some thermodynamic properties calculations are performed for polar and non-polar substances. The properties included are vapor pressure, saturated liquid volume, molar volume in the single phase region and heat capacity at constant pressure. The performance of the model is compared with the original Peng–Robinson EoS [11], a generalized Peng–Robinson–Stryjek–Vera EoS developed by Figueira et al. [20] and a modified three-parameters EoS developed recently by the authors [46,47].

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