Fluid Phase Equilibria 408 (2016) 58–71

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

# An evolved cubic equation of state with a new attractive term

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ARTICLE INFO

*Article history:*
Received 20 May 2015
Received in revised form
12 August 2015
Accepted 13 August 2015
Available online 17 August 2015

*Keywords:*
Vapor pressure
Equation of state
α-Function
Peng–Robinson EOS
Reservoir fluids
Petroleum fractions

ABSTRACT

A large variety of modifications have been presented for the temperature dependent function (α) existing in the attractive term of cubic equations of state (CEOS). Most of α-functions attempted to modify the vapor pressure prediction of polar components while other modifications have focused on both polar and non-polar compounds and other relations have considered an expansion of polynomials in the acentric factor ($\omega$) and reduced temperature ($T_r$) to predict vapor pressure more accurately. In most cases such as Soave and Peng–Robinson equations of state, the suggested α-functions do not show a limiting behavior when temperature increases infinitely. In addition, the incompetency of many α-functions in describing the supercritical behavior of fluids have been modified by defining specific parameters for some different components or switching α-functions. Such approaches can create difficulties for the calculation of properties in which, there are equations of state derivatives. In this work, a new α-function has been put forward to improve the attractive term of Peng–Robinson EOS. The proposed model is capable of predicting the saturation vapor pressure of light gases, polar, nonpolar and heavy hydrocarbon compounds. The normal boiling point ($T_b$) is used as an additional parameter along with acentric factor ($\omega$) and reduced temperature ($T_r$) to enhance the ability of the proposed α-function in the prediction of fluid phase behavior especially for petroleum fractions and heavy cuts existing in reservoir fluids samples. Moreover, two discriminating indexes ($\lambda_1$, $\lambda_2$) are introduced, to handle all pure substances and classify them under distinct groups for the allocation of special coefficients to each group. Experimental vapor pressure of 31 different pure components, 11 binary mixtures and 12 reservoir oil samples were collected, in order to evaluate the performance of the proposed model compared to the original Peng–Robinson. A comparison between the proposed model and other powerful equations of state such as modified PR, PSRK and PC-SAFT model was also performed, and the results of which indicate that the new proposed model has better outcomes over the mentioned methods, especially for complex mixtures and reservoir fluids. Furthermore, the proposed α-function shows a reasonable limiting behavior as the temperature approaches infinity and is capable of describing the fluid phase behavior at supercritical region.



## 1. Introduction

Equations of state are of specific importance in chemical engineering design, especially in the study of the phase equilibria and describing thermodynamic properties of pure substances and fluid mixtures. Initially, equations of state were applied for pure substances but they have improved rapidly in the prediction of phase behavior in non-polar and polar mixtures. The merits of using equations of state is their capability to calculate phase equilibria over wide ranges of temperature and pressure in mixtures of different components, from light gases to heavy liquids. They can also be used for the prediction of vapor–liquid, liquid–liquid and supercritical fluid phase equilibria. A large number of equations of state have been suggested in the literature with either an empirical, semi-empirical or theoretical basis. In spite of the recent development of molecular-based equations of state such as statistical association fluid theory (SAFT) [1–2], the simplicity and popularity of cubic equations of state (CEOS) lead to the continuation of their improvements. Van der Waals equation of state [3] was the first equation to predict vapor–liquid coexistence. Although Van der Waals equation was not accurate for most applications, it attracted

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http://dx.doi.org/10.1016/j.fluid.2015.08.013
0378-3812/

**Nomenclature**

| | |
|---|---|
| $a_1$, $a_2$, $a_3$, $a_4$, $b_1$, $b_2$, $b_3$, $c_1$, $c_2$ and $d$ | adjustable variables used in Eqs. (9)–(11) |
| $a$ | attraction parameter |
| $a_c$ | constant parameter defined by Eq. (6) |
| $A$ | dimensionless parameter defined by Eq. (26) |
| AAD% | average absolute percent deviation |
| $b$ | van der Waals co volume |
| $B$ | dimensionless parameter defined by Eq. (27) |
| $B_o$ | oil formation volume factor |
| $C_P$ | specific heat capacity |
| GOR | gas oil ratio |
| $M_w$ | molecular weight |
| OF | objective function |
| $P$ | pressure |
| $R$ | gas constant |
| SG | specific gravity |
| $T$ | temperature |
| $v$ | specific molar volume |
| $x$ | mole fraction |
| $Z$ | compressibility factor |

*Greek letters*

| | |
|---|---|
| $\alpha$ | temperature dependent function in the attractive term |
| $\beta$ | temperature dependent function defined by Eq. (10) |
| $\gamma$ | temperature dependent function defined by Eq. (11) |
| $\lambda_1$ | index of discrimination |
| $\lambda_2$ | index of discrimination |
| $\xi$ | a variable which can be substituted by Mw or Tb in Eq. (16) |
| $\rho$ | density |
| $\phi$ | fugacity coefficient |
| $\Phi$ | a variable which can be substituted by any of the critical properties in Eq. (15) |
| $\omega$ | acentric factor |

*Subscripts*

| | |
|---|---|
| $A$ | attraction |
| $b$ | normal boiling point (for temperature) and bubble point (for pressure) |
| $br$ | reduced normal boiling point |
| $c$ | critical property |
| $i$, $j$ | property of component $i$, $j$ |
| $L$ | liquid |
| max | maximum |
| $r$ | reduced property |
| $R$ | repulsion |
| sat | saturation |

*Superscripts*

| | |
|---|---|
| calc | calculated |
| exp | experimental |
| $'$ | first derivative |
| $''$ | second derivative |
| $*$ | ideal gas state |
| ^ | partial property in the mixture |

great attentions to this field because it was the first effort to describe the real PVT behavior of fluids. Later on, Redlich–Kwong equation of state [4] improved the precision of van der Waals equation by modifying the attractive term through defining a temperature dependent function. Soave [5] and Peng and Robinson [6] proposed considerable modifications for Redlich–Kwong equation to improve the predictions of volumetric, thermodynamic, and phase equilibrium properties such as vapor pressure, liquid density, and equilibria ratios. Other modifications have also been presented for the repulsive term by Carnahan and Starling [7], Guggenheim [8] and Boublik [9]. Christoforakos and Franck [10] improved both the attractive and repulsive terms of van der Waals equation of state. Capability of a cubic equation of state to calculate phase equilibria of mixtures depends upon the accuracy of predicting pure component vapor pressures. A significant part of attempts for improving the precision of cubic equations of state has been devoted to the enhancement of the temperature dependent attractive term, through the amending α-function. A variety of modifications have been proposed for the temperature-dependent function $\alpha\ (T_r, \omega)$ existing in the attractive term of the SRK and PR equations to improve correlations and predictions of vapor pressure for diverse fluids. Table 1 presents a summary of expressions previously reported in the literature for temperature dependent function. Most of the proposed α-function models are related to modifying the vapor pressure estimation of polar components. Some modifications have focused on both polar and non-polar compounds while other developments have applied an expansion of polynomials in the acentric factor $(\omega)$ or reduced temperature to predict vapor pressure more accurately. In most cases, the proposed α-functions do not abide by a limiting behavior when the temperature increases infinitely (such as Soave and Peng–Robinson α-functions). Furthermore many α-functions suffer from incompetency to describe supercritical behavior precisely. This problem has been remedied by presenting specific parameters for different components or changing α-functions. Such methods can lead to difficulties in derivative properties. Hence, a generalized function is more desirable than defining component-dependent parameters in α-function. On the other hand the bubble pressure of complex mixtures containing ambiguous fractions with non-distinguishable nature (such as petroleum fractions in reservoir fluids) is deeply affected by the accurate estimation of α-function for pure substances and petroleum fractions. A petroleum fraction includes a large number of various unspecified hydrocarbon components with unknown composition. Several correlations have been proposed by Twu [43], Kesler and Lee [44], Riazi and Daubert [45], and Hosseinifar and Jamshidi [46], to characterize petroleum fractions for the estimation of their physical and critical properties (critical temperature, critical pressure and acentric factor). Applying an accurate correlation to predict the acentric factor for petroleum fractions can have a major influence on the prediction of bubble pressure in the mixture in those methods using the acentric factor to estimate α-function. In this study, we concentrate our attention on the attractive term of Peng–Robinson equation of state to overcome all the aforementioned defects. The main purpose for the development of the new suggested model is obtaining a generalized and enhanced expression for the temperature dependent function existing in PR EOS, which is capable of covering all types of pure substances. One of the major problems with the former expressions for the prediction of α-function is their inability to cover wide ranges of miscellaneous pure substances. Due to this restriction, several functions have been proposed in which the model adjustable parameters are tuned to the experimental data of a particular group. In the proposed model, two useful discriminating indexes $(\lambda_1, \lambda_2)$ are introduced to handle all pure substances and classify them under distinct groups. In the next step, the adjustable parameters of the proposed model are determined for each particular group using an appropriate optimization method. Based on this approach, the proposed model will be applicable to different