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A consistent and precise alpha function for cubic equations of state

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ABSTRACT

Generalized form of alpha function to acentric factor is established for alpha function introduced in our recent study (P. Mahmoodi, M. Sedigh, Second derivative of alpha functions in cubic equations of state, J. Supercrit. Fluids. (2016). doi:10.1016/j.supflu.2016.05.012.). It is shown that proposed generalized alpha function meet all suggested criteria of consistent alpha function by Le Guennec et al. and also it gives correct predictions for C_v and C_p values. Moreover in subcritical and supercritical temperature ranges thermodynamic packages (combination of a CEoS and an alpha function) with the proposed alpha function have superior accuracy.

Eventually, results demonstrate that thermodynamic package consist of the SRK EoS, the proposed generalized form of alpha function in this study and classical mixing rule by binary interactions hired from PPR78, is very accurate in vapor-liquid equilibria prediction of highly asymmetrical hydrocarbon mixtures.

1. Introduction

In calculation of phase behavior and thermodynamic properties of fluids, the Soave–Redlich–Kwong (SRK) [1] and the Peng–Robinson (PR) [2] cubic equations of state are widely used and gave birth to well-established predictive models like PPR78 [3–5], PR2SRK [6], NRTL-PR [7,8], VTPR [9] and UMR-PR [10]. These equations are categorized as two-parameter cubic equations of state and can be expressed by:

$$p = \frac{RT}{v-b} - \frac{a_c\,\alpha(T_r)}{(v+c_1 b)(v+c_2 b)} \tag{1}$$

where P is the pressure, R the gas constant, T the temperature, v the molar volume, a_c, $\alpha(T_r)$ and b are the EOS parameters. In this equation c_1 and c_2 are two constants which have different values for each cubic equation of state. For the SRK equation ($c_1 = 0$ and $c_2 = 1$) and for the PR equation ($c_1 = 1-\sqrt{2}$, $c_2 = 1 + \sqrt{2}$). $\alpha(T_r)$ in Eq. (1) stands for alpha function.

1.1. The soave type alpha function and consistency of alpha functions

The Soave type alpha function is:

$$\alpha(T_r) = \left(1 + m\left(1 - \sqrt{T_r}\right)\right)^2 \tag{2}$$

where m is a second order polynomial function of the acentric factor. For the original SRK [1] and PR [2] and PR78 [7] equations are as following:

$$m_{SRK} = 0.480 + 1.574\omega - 0.176\omega^2 \tag{3}$$

$$m_{PR} = 0.37464 + 1.54226\omega - 0.26992\omega^2 \tag{4}$$

$$m_{PR78} = 0.37464 + 1.54226\omega - 0.26992\omega^2, \quad \omega \le 0.491 \tag{5}$$

$$m_{PR78} = 0.379642 + 1.48503\omega - 0.164423\omega^2 + 0.016666\,\omega^3, \quad \omega > 0.491 \tag{6}$$

Since the original paper by Soave, many modifications of alpha functions were published in order to increase the accuracy of cubic EoSs [12–18]. In the study conducted by authors [19], it was highlighted that the abnormal minimum exhibited by the Soave

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alpha function at high reduced temperatures has negligible effect on the calculated thermodynamic properties. Thus the Soave equation can *indeed* be considered a consistent alpha function. According to previous studies [19–22] Consistency in terms of alpha function means that the alpha functions shall fulfill the following conditions:

- Alpha function shall be equal to one at critical temperature.
- Alpha function shall be positive, continuous and monotonic at all temperature ranges.
- First and second derivatives of the alpha function shall be continuous and monotonic at all temperature ranges.
- Thermodynamic packages (CEoSs with alpha functions) in calculation of thermodynamic properties such as enthalpy, C_v and C_p in subcritical and supercritical temperatures shall have correct trend and reasonable accuracy.

Le Guennec et al. [23] redefined the terms of consistency for alpha functions by adding a new condition for third derivative of the alpha function. Based on the study by Le Guennec et al. [23] a consistent alpha function shall meet all of following conditions:

- $\alpha(T_r) \geq 0$ and $\alpha(T_r)$ is continuous
- $\frac{d\alpha(T_r)}{dT_r} \leq 0$ and $\frac{d\alpha(T_r)}{d(T_r)}$ is continuous
- $\frac{d^2\alpha(T_r)}{dT_r^2} \geq 0$ and $\frac{d^2\alpha(T_r)}{dT_r{}^2}$ is continuous
- $\frac{d^3\alpha(T_r)}{dT_r^3} \geq 0$

Due to high risk of errors in prediction of thermodynamic properties using of CEoSs with inconsistent alpha function is not recommended in thermodynamic calculations. However, inconsistency of the Soave alpha functions as an exception doesn't make any problem in thermodynamic calculations. On the other hand, the Soave alpha function that has only one adjustable parameter has not good accuracy in correlation of vapor pressures of polar compounds, heavy hydrocarbons and other complex pure compounds. For these kinds of compounds using of alpha functions with two or more parameters seems to be needed. Unfortunately recent studies showed most of existing alpha functions with more than one adjustable parameters are not consistent [20,23]. Thus for more accurate vapor pressure correlation without causing any inconsistency, introducing of consistent alpha functions with 2 or 3 adjustable parameters are essentially needed.

As it will be discussed in the next section, lately authors developed two consistent alpha functions by 2 and 3 individual adjustable parameters [20]. That study demonstrated that, these equations were the only consistent alpha functions that have reasonable accuracy for different kinds of compounds including polar compounds. A few later, a consistent alpha functions with 3 adjustable parameters by defining constrains for adjustable parameters of Twu et al. alpha function is developed by Le Guennec et al. [23]. This consistent alpha function with individual parameters has good accuracy for polar and complex compounds. For generalized form of alpha function most recently Le Guennec et al. [24] developed a consistent alpha function based on Twu88 [25] model. The Le Guennec et al. consistent general alpha function although demonstrates better correlation for saturated isobar heat capacity of pure compounds, respect to the Soave alpha function, it does not show impressive improvement in vapor pressure correlations.

This study aims to develop consistent generalized form of alpha function for the PR and SRK equations. It is necessary that the proposed alpha functions have decent accuracy for heavy normal alkanes to overcome the limitation of generalized form of the Soave equation.

1.2. General Twu et al. alpha function

Twu et al. [15,16] defined their generalized form of alpha function as linear function of acentric factor by following Pitzer's corresponding states principle as:

$$\alpha(T_r) = \alpha(T_r)^0 + \omega\left(\alpha(T_r)^1 - \alpha(T_r)^0\right) \tag{7}$$

where the $\alpha0$ and $\alpha1$ are alpha functions with following formulation:

$$\alpha(T_r) = T_r{}^{N(M-1)} exp\left[L\left(1 - T_r{}^{NM}\right)\right] \tag{8}$$

In our previous study [20] and in the study by Neau et al. [21,22], it was shown that second derivative of the Twu et al. alpha function respect to temperature is not monotonically decreasing and calculated constant pressure and volume heat capacities by this function are not accurate.

1.3. Coquelet et al. alpha function

By combining Mathias–Copeman [27] and Trebble–Bishnoi [28] models, Coquelet et al. [14] proposed the following alpha function:

$$\alpha(T_r) = exp[C_1(1 - T_r)] \times \left(1 + C_2\left(1 - \sqrt{T_r}\right)^2 + C_3\left(1 - \sqrt{T_r}\right)^3\right)^2 \tag{9}$$

For $T_r > 1$ the Trebble–Bishnoi [28] alpha function is used:

$$\alpha(T_r) = exp[C_1(1 - T_r)] \tag{10}$$

Coquelet et al. proposed generalized form of their alpha function through correlating the parameters C_1, C_2 and C_3 as second polynomial function of acentric factor [14].

1.4. Exponential alpha function by means of a Taylor series of Soave relation

In our recent study [20] second derivative of Coquelet et al. alpha function with four other well-established alpha functions (Mathias–Copeman [26], Twu et al. [15,16], Stryjek–Vera [13] and Heyen [28]) for cubic equations of state are investigated. It was demonstrated that second derivatives of these alpha functions are not totally consistence. Discontinuity of the second derivatives of the Mathias–Copeman and the Coquelet et al. alpha functions at critical temperature are major highlighted unusual behaviors of these alpha functions in our previous paper [20]. At that study two new alpha functions derived from Taylor expansion of the Soave alpha function which have proper derivatives are proposed. Development of these models was started by taking the natural logarithm of both side of Eq. (2):

$$\ln \alpha(T_r) = 2 \times \ln(1 + X), \quad where\ X = m\left(1 - \sqrt{T_r}\right) \tag{11}$$

The Taylor series of the function ln (1 + X) is:

$$\ln(1 + X) = X - \frac{1}{2}X^2 + \frac{1}{3}X^3 - \frac{1}{4}X^4 + \ldots, \quad when\ -1 < X \leq 1 \tag{12}$$

From triple point temperature to critical temperature for all of the components $X = m(1-T_r^{0.5})$ is in the range [−1 1]. Consequently,