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# A modification of the alpha function ($\alpha$), and the critical compressibility factor ($\zeta_c$) in ER (Esmaeilzadeh–Roshanfekr) equation of state

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ABSTRACT

In this study a temperature-dependent function of the attractive term, called the alpha function, and the critical compressibility factor ($\zeta_c$) of the ER (Esmaeilzadeh–Roshanfekr) equation of state have been modified to improve the performance of equation of state. The ER EOS is a new three-parameter equation of state that was developed in 2006 with special attention to application for reservoir fluids. Using these modifications, saturated liquid density, saturated vapor density and vapor pressure of pure components are calculated more accurate than the ER equation of state. The average absolute deviations of the predicted saturated liquid density, saturated vapor density and vapor pressure of pure components with the modified ER (mER) are 0.95%, 1.17% and 1.20%, respectively. Also, the mER, the ER and the Peng–Robinson (PR) equation of state are used to predict dew point pressure for six gas condensate mixtures and bubble point pressure for five LNG mixtures. In order to have an unbiased comparison between these equations of state, van der Waals mixing rules are used without using any adjustable parameters ($k_{ij} = 0$). The results show that the mER EOS predicts the dew point pressure and bubble point pressure with best accuracy among the other EoSs.

## 1. Introduction

Equations of state are applied in many industries including separation, oil and gas industry, supercritical extraction, etc. van der Waals [1] developed the first cubic equation of state that is a two-parameter equation. In this equation of state, the effect of intermolecular forces and size of molecules are considered. Redlich and Kwong [2] modified the attractive term of van der Waals equation of state. Soave [3] and Peng–Robinson [4] proposed an equation of state that the parameters were defined as functions of reduced temperature and acentric factor. Both of these equations assume a fixed value of the critical compressibility factor (0.302 and 0.333) for all substances and, as a result, the predicted values for saturated liquid density differ considerably from their experimental values. On the other hand, some equations of state proposed by Schmit and Wenzel [5] and Patel and Teja [6] introduced a third parameter to their equations. This suggestion led to the introduction of a substance-dependent critical compressibility which allowed them to reproduce more accurately the experimental saturate liquid density at a particular temperature. Their works showed that the optimum value of substance critical compressibility, $\zeta_c$, was not equal to the experimental critical compressibility of the fluid of interest. However, none of them could predict liquid density and phase behavior of heavy hydrocarbons with acceptable accuracy. Recently, Esmaeilzadeh–Roshanfekr (ER) [7] developed a new cubic EOS with special attention to the application for reservoir fluids. This equation of state, in addition to the critical temperature, $T_c$, and the critical pressure, $P_c$, requires $\zeta_c$, $m_1$ and $m_2$, as an input parameter. Where, $\zeta_c$ was treated as an empirical parameter. The value of $\zeta_c$ was found to be a function of temperature at some reduced temperatures. They observed that, the value of $\zeta_c$ for components is constant up to a certain point (called $T_r'$) and after that becomes a function of temperature. In order to generalize this equation of state, the values of the parameters $\zeta_c$, $m_1$ and $m_2$ have been correlated with the acentric factor. A detailed description of the ER EOS can be found in the paper of Esmaeilzadeh and Roshanfekr [7]. The authors used the ER EOS to predict the PVT properties of gas condensate reservoir fluids [8]. The obtained results show that this equation of state has less deviation than the PR EOS that is usually used to predict the phase behavior of petroleum mixture. In this work, the temperature dependence of the attractive

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term, $\alpha(T)$, and the critical compressibility factor, $\zeta_c$, of the ER (Esmaeilzadeh–Roshanfekr) equation of state have been modified. We shall demonstrate the ability of the modified ER (mER) EOS to predict the saturated liquid density, saturated vapor density and vapor pressure of pure components with respect to other equations of state (ER, PTV [9], PT and PR). Also, dew point pressure and bubble point pressure of some mixtures are calculated with the modified ER EOS. The results of the mER are remarkable with respect to the ER and PR EOS.

## 2. The ER equation of state

The ER equation of state (EOS) [7] is a three-parameter EOS which has the following form:

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+c)+c(v-c)} \tag{1}$$

where $R$ is the universal gas constant, $a$ is a function of temperature and $b$ and $c$ are constants. For a pure compound

$$a(T) = \Omega_{\rm a}\left(\frac{R^2\times T_{\rm c}^2}{P_{\rm c}}\right)\alpha(T_{\rm r}) \tag{2}$$

$$b = \Omega_{\rm b}\left(\frac{RT_{\rm c}}{P_{\rm c}}\right) \tag{3}$$

$$c = \Omega_{\rm c}\left(\frac{RT_{\rm c}}{P_{\rm c}}\right) \tag{4}$$

where,

$$\Omega_{\rm b} = 2\Omega_{\rm c} - 1 + 3\xi_{\rm c} \tag{5}$$

$$\Omega_{\rm a} = 3\xi_{\rm c}^2 + \Omega_{\rm c}^2 + 2\Omega_{\rm b}\Omega_{\rm c} + 2\Omega_{\rm c} \tag{6}$$

and $\Omega_c$ is the smallest positive root of the cubic:

$$\Omega_{\rm c}^3 + (3\xi_{\rm c} - \tfrac{5}{8})\Omega_{\rm c}^2 + (3\xi_{\rm c}^2 - \tfrac{3}{4}\xi_{\rm c})\,\Omega_{\rm c} + (\xi_{\rm c}^3 - \tfrac{3}{8}\xi_{\rm c}^2) = 0 \tag{7}$$

the following function has been used for $\alpha(T_{\rm r})$:

$$\alpha = [m_1 + m_2(1 - T_{\rm r}^{0.5})]^2 \tag{8}$$

In Eqs. (5)–(8), the values of the parameters $\zeta_c$, $m_1$ and $m_2$ have been correlated with the acentric factor. The resulting correlations are given by

$$\zeta_{\rm c} = 0.3284438 - 0.0690264\omega + 0.0078711\omega^2 \tag{9}$$

$$m_1 = 0.999035 - 0.01061842\omega - 0.0081174\omega^2 \tag{10}$$

$$m_2 = 0.4400108 + 1.5297151\omega - 0.4710752\omega^2 \tag{11}$$

$\zeta_{\rm c}$ was calculated by Esmaeilzadeh and Roshanfekr [7] as follows:

For $T_{\rm r} < T_r'$:

$\zeta_{\rm c}$ is obtained from Eq. (9).

For $T_{\rm r} > T_r'$:

$$\xi_{\rm c}' = \xi_{\rm c} - (\xi_{\rm c} - Z_{\rm c})\left(\frac{T_r' - T_{\rm r}}{T_r' - 1}\right)^2 \tag{12}$$

where

$$T_{\rm r}' = 0.789216 + 0.1585581\omega - 0.133193\omega^2 \tag{13}$$

For heavy hydrocarbons, $Z_{\rm c}$ can be obtained from the Nath correlation [10] as follows:

$$Z_{\rm c} = 0.2918 - 0.0928\omega \tag{14}$$

To predict mixture properties, the following van der Waals mixing rules are used

$$b = \sum_j x_j b_j \tag{15}$$

and

$$a = \sum_i \sum_j x_i x_j a_{ij} \tag{16}$$

where

$$a_{ij} = \sqrt{a_{ii}a_{jj}}(1 - k_{ij}) \tag{17}$$

The fugacity coefficient for component $i$ in a mixture is calculated from:

$$\ln\hat{\phi}_i = \frac{b_i}{b}\left(\frac{B}{Z-B}\right) - \ln(Z-B) - \frac{A}{2\sqrt{2}C}\left(\frac{2\sum_j x_j a_{ij}}{a} - \frac{c_i}{C}\right)\ln\left(\frac{Z+2\sqrt{2}C}{Z-2\sqrt{2}C}\right) + \frac{c_i}{C}\left(Z - \frac{Z}{Z-B}\right) \tag{18}$$

where $Z$ is the compressibility factor, $A = ap/(R^2T^2)$, $B = bp/RT$ and $C = cp/RT$.

## 3. The modified ER equation of state

The temperature dependence of the attractive term, $\alpha(T)$, and the critical compressibility factor, $\zeta_{\rm c}$, of the ER (Esmaeilzadeh–Roshanfekr) equation of state have been modified to improve the performance of the ER EOS for the prediction of PVT properties of pure and mixture components.

For the 24 components studied in this work, at each temperature the values of $\alpha(T)$ and $\zeta_{\rm c}$ were obtained by minimizing the following objective function:

$$\Omega = \left(w_1\frac{\left|P_{{\rm cal},j}^v - P_{{\rm exp},j}^v\right|}{P_{{\rm exp},j}^v} + w_2\frac{\left|\rho_{{\rm cal},j}^l - \rho_{{\rm exp},j}^l\right|}{\rho_{{\rm exp},j}^l}\right) \tag{19}$$

with $w_1 = 0.8$ and $w_2 = 0.2$. The physical properties of these components are listed in Table 1.

For the present study, the Genetic Algorithm in MATLAB environment has been used to minimize the objective function. By this technique, the values of $\alpha(T)$ and $\zeta_{\rm c}$ can be obtained simultaneously.

### 3.1. Evaluation of $\zeta_c$

We observed as the Esmaeilzadeh–Roshanfekr that, the value of $\zeta_{\rm c}$ for components is constant up to a certain point (called $T_{\rm r}'$) and after that becomes a function of temperature.

As shown in Fig. 1, the value of $\zeta_{\rm c}$ changes from the calculated value to the experimental value ($Z_{\rm c}$) as $T_{\rm r}$ changes from $T_{\rm r}'$ to 1. In the region, where $\zeta_{\rm c}$ is a function of temperature ($T_{\rm r} > T_{\rm r}'$), its temperature dependency can be divided into two regions. In the region where ($T_{\rm r}' < T_{\rm r} < 0.9$) the temperature dependency of $\zeta_{\rm c}$ was found to be a quadratic function of temperature and in the region where ($0.9 < T_{\rm r} < 1.0$) the temperature dependency was found to be a linear function of temperature (also, Patel and Teja [6] used a linear function of temperature in this region).