



Prediction of vapor–liquid equilibrium data of the system MTBE + methanol + ethanol by PRSV2 EOS

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ABSTRACT

The Stryjek and Vera (1986) [9] modification of Peng–Robinson (PRSV2) equation of state has been applied for modeling vapor–liquid equilibrium of the systems MTBE + methanol, MTBE + ethanol and methanol + ethanol. Binary interaction parameters for mixing rules have been estimated by using experimental data at the atmospheric pressure. The calculated binary interaction parameters were used for predicting azeotropic behavior at high pressure and also for isobaric equilibrium points which showed an excellent agreement with experimental data. In addition, estimated binary interaction parameters for binary systems were used for ternary system (MTBE + methanol + ethanol). The predictions deviated only slightly from the experimental data. The results show PRSV2 can be used for VLE prediction of polar systems.

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1. Introduction

Tertiary-alkyl ethers are low toxic and low polluting oxygenated petrochemical compounds, used as an octane booster for lead-free or low-leaded gasoline and also increasingly valued as solvents and as chemical reactants [1,2].

In recent years, increasing use of ethers as oxygenated additives for gasoline has necessitated large increases in worldwide ether production, with important implications for the hydrocarbon processing industry. The ether most widely added to gasoline is 2-methoxy-2-methylpropane (more commonly MTBE, methyl tert-butyl ether). These ethers are used in combination with methanol and ethanol co-solvents as octane-enhancing agents and anti-pollutants in gasoline blends [1]. The thermodynamics of ether + alcohol mixtures are thus of some interest [3]. In the literature vapor–liquid equilibrium (VLE) measurements for MTBE + methanol, MTBE + ethanol and methanol + ethanol mixtures were correlated using the Wilson [23], NRTL [24], and UNIQUAC [25] models for the liquid phase and the equation of ideal state for the vapor phase [4–8]. The equation of the ideal state for the vapor phase in high pressure cannot predict the behavior of the vapor phase accurately.

For system of strongly non-ideal at high pressures, the ideal conditions for vapor phase or simple cubic equations of state (EOS) cannot be applied for correlating vapor liquid equilibrium data. But, using more appropriate and somewhat complicated mixing rules for different types of mixture in simple cubic EOS provide high capability for these EOS in vapor–liquid equilibrium calculations. So, ‘fugacity coefficient–fugacity coefficient’ approach for vapor and liquid could be used instead of the ‘activity coefficient–fugacity coefficient’ approach, i.e., using an excess Gibbs energy model for the liquid phase and an equation of state for the vapor phase.

A modification of the Peng–Robinson equation of state [12] has been discussed by Stryjek and Vera [9]. This modification, called the PRSV equation of state, contains one adjustable parameter per pure compound and represents vapor pressure data with high accuracy. Stryjek and Vera have used their modified equation to correlate vapor–liquid equilibrium data of hydrochloric acid solutions [10]. Vera has added two additional parameters for higher accuracy in PVT prediction for pure component and has called it PRSV2 [11].

In this article the behavior of the vapor–liquid equilibrium of MTBE + methanol, MTBE + ethanol and methanol + ethanol systems has been modeled by the PRSV2 EOS. Then, by using the six obtained binary interaction coefficients and suitable mixing rules the potential of the PRSV2 equation of state for correlating the vapor–liquid equilibrium of ternary system (MTBE + methanol + ethanol) has been illustrated. The PRSV2 equation, using six adjustable parameters, gives an excellent representation of this system containing a strong polar component.

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2. Theory

2.1. The PRSV2 equation of state

The PRSV2 equation of state retains the basic form of the Peng–Robinson equation [12]

$$P = \frac{RT}{v-b} \frac{a}{v^2 + 2bv - b^2} \quad (1)$$

with

$$a = \left(\frac{0.45724R^2T_c^2}{P_c} \right) \alpha \quad (2)$$

and

$$b = \frac{0.0778RT_c}{P_c} \quad (3)$$

where

$$\alpha = [1 + k(1 - T_R^{0.5})]^2 \quad (4)$$

Peng and Robinson considered k to be a function of the acentric factor only. The PRSV2 equation considers k to be function of acentric factor and reduced temperature of the form:

$$k = k_0 + [k_1 + k_2(k_3 - T_R)(1 - T_R^{0.5}) \times (1 + T_R^{0.5})(0.7 - T_R)] \quad (5)$$

where k_0 is given by

$$k_0 = 0.378893 + 1.4897153\omega - 0.1731848\omega^2 + 0.0196544\omega^3 \quad (6)$$

And k_1 , k_2 and k_3 are pure compound adjustable parameters. The values of k_1 , k_2 and k_3 for MTBE, methanol and ethanol have been reported by Vera [11,13].

As observed before, the Peng–Robinson equation is applicable only for hydrocarbons and slightly polar compounds at reduced temperatures of about 0.7 and above, while the PRSV2 equation is applicable for all compounds independent of their size, shape, polarity or degree association [11].

2.2. The mixing rules for vapor–liquid equilibrium calculations

In this work we use the conventional mixing rules,

$$b = \sum_i x_i b_i \quad (7)$$

and

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad (8)$$

The fugacity coefficient of a component i in a multi component mixture takes the form [11]:

$$\ln \varphi_i = \frac{b_i}{b}(z-1) - \ln(z-B) - \frac{A}{2\sqrt{2}B} \times \left(\frac{\bar{a}_i}{a} + 1 - \frac{b_i}{b} \right) \ln \frac{z + (1 + \sqrt{2})B}{z + (1 - \sqrt{2})B} \quad (9)$$

with

$$\bar{a}_i = \left(\frac{\partial na}{\partial n_i} \right)_{n_j \neq i} \quad (10)$$

For convenience, \bar{a}_i has been left unspecified in Eq. (8) since its final form depends on the assumption made regarding the cross term a_{ij} . The following expression for the cross term a_{ij} gives satisfactory results.

Table 1

Binary parameters for the system MTBE(1)+methanol(2)+ethanol(3).

$k_{12} = 6.385 \times 10^{-4}T(K) - 0.175$	$k_{21} = 5.479 \times 10^{-4}T(K) - 0.235$
$k_{13} = 5.803 \times 10^{-4}T(K) - 0.149$	$k_{31} = 4.17 \times 10^{-4}T(K) - 0.152$
$k_{23} = 9.446 \times 10^{-5}T(K) - 0.03$	$k_{32} = -0.00638$

For a binary mixture of components i and j , Margules-type two-binary-parameter has the following form [11],

$$a_{ij}(a_{ii}a_{jj})^{0.5}(1 - x_i k_{ij} - x_j k_{ji}) \quad (11)$$

where $a_{ij} = a_{ji}$, but $k_{ji} \neq k_{ij}$.

Using Eqs. (9)–(11) as mixing rules, the fugacity coefficient for component i in a binary mixture of components i and j , takes the form

$$\ln \varphi_i = \frac{b_i}{b}(z-1) - \ln(z-B) - \frac{A}{2\sqrt{2}B} \times \left[\frac{2}{a} (x_i a_{ii} + x_j a_{ij} + x_i x_j^2 \sqrt{a_{ii}a_{jj}}(k_{ji} - k_{ij})) - \frac{b_1}{b} \ln \frac{z + (1 + \sqrt{2})B}{z + (1 - \sqrt{2})B} \right] \quad (12)$$

In addition, for component i in a ternary mixture including i , j and k , fugacity coefficient has been obtained as follows

$$\ln \varphi_i = \frac{b_i}{b}(z-1) - \ln(z-B) - \frac{A}{2\sqrt{2}B} \left\{ \frac{2}{a} [x_i a_{ii} + x_j a_{ij} + x_k a_{ik} + x_j x_k \sqrt{a_{jj}a_{kk}}(x_j k_{jk} + x_k k_{kj}) + x_i x_j \sqrt{a_{ii}a_{jj}}(x_i k_{ij} + x_j k_{ji} - k_{ij}) + x_i x_k \sqrt{a_{ii}a_{kk}}(x_i k_{ik} + x_k k_{ki} - k_{ik})] - \frac{b_i}{b} \right\} \ln \frac{z + (1 + \sqrt{2})B}{z + (1 - \sqrt{2})B} \quad (13)$$

As Eq. (13) depicts for binary system there are two interaction parameters and for ternary system there are six interaction parameters in the fugacity coefficient equation exists. Eq. (13) reduced to Eq. (12) when $x_k = 0$.

3. Results and discussion

3.1. Estimation of binary interaction parameters

For vapor and liquid phases in equilibrium, the criterion of equilibrium is as follows:

$$y_i = \frac{x_i \varphi_i^l}{\varphi_i^v} \quad (14)$$

where x_i and y_i are the mole fraction of component i in the liquid and vapor phases respectively.

The experimental isobaric VLE compositions of MTBE+methanol, MTBE+ethanol and methanol+ethanol systems at atmospheric pressure were extracted from literature [14,15], then by using these experimental data and the method of algorithm genetic the best fitted interaction parameters have been found in different temperatures in such a way that the minimum deviations from experimental data have been raised. In the next step, these interaction parameters have been fitted in terms of temperature, the results are shown in Table 1. These expressions for binary interaction parameters that are function of temperature were used in Eq. (11) for calculating a_{ij} . All the experimental VLE data were thermodynamically consistent by the PRSV2 EOS as have been shown in Fig. 1. In this figure the experimental isobaric VLE compositions for MTBE+methanol, MTBE+ethanol and methanol+ethanol systems have been compared with the predicted values of PRSV2 EOS with the obtained

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