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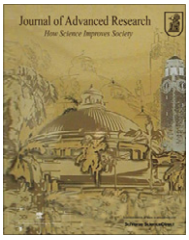

ORIGINAL ARTICLE

Semi-empirical correlation for binary interaction parameters of the Peng–Robinson equation of state with the van der Waals mixing rules for the prediction of high-pressure vapor–liquid equilibrium

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Abstract Peng–Robinson equation of state is widely used with the classical van der Waals mixing rules to predict vapor liquid equilibria for systems containing hydrocarbons and related compounds. This model requires good values of the binary interaction parameter k_{ij}. In this work, we developed a semi-empirical correlation for k_{ij} partly based on the Huron–Vidal mixing rules. We obtained values for the adjustable parameters of the developed formula for over 60 binary systems and over 10 categories of components. The predictions of the new equation system were slightly better than the constant-k_{ij} model in most cases, except for 10 systems whose predictions were considerably improved with the new correlation.

Introduction

The use of simple equations of state for the calculations of Vapor–Liquid Equilibrium (VLE) is preferred by practicing engineers over the use of more complicated models [1]. Cubic equations of state have gained overwhelming acceptance as a robust and reliable, yet relatively simple, model for predicting VLE of high-pressure systems. Mixing rules are used in conjunction with cubic equations of state for the complete representations of fluid mixtures. These mixing rules require empirically-determined Binary Interaction Parameters (BIPs) to describe the VLE more accurately. The lack of those binary interaction parameters often result in inaccurate VLE predictions.

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Nomenclature

A	equation of state parameter
b	equation of state parameter
K	Kelvin
k_{ij}	binary interaction parameters, dimensionless
OF	objective function
P	absolute pressure, bar
Pxy	a phase diagram that has pressure on its y-axis and both the liquid composition (x) and the vapor composition (y) on its x-axis.
R	Universal gas constant, 8.314 m^3 Pa/K mole
RMSE	Root Mean Square Error
T	absolute temperature, K
V	molar volume, m^3/mole
x	liquid phase mole fraction
x_i	liquid phase mole fraction of ith component
y	vapor phase mole fraction
Z	compressibility factor

Greek letters

$\hat{\varphi}_i$	fugacity coefficient of ith component
γ_i	activity coefficient of ith component
θ_1, θ_2, θ_3	adjustable parameters, dimensionless

Superscript

E	excess property
∞	at infinite pressure
V	vapor phase property
L	liquid phase property

The experimental data needed for the generation of BIPs may be difficult or too costly to obtain. Thus, the development of simple models for the prediction of high-pressure VLE with no need for experimental data is an important research objective. Several successful attempts have been made to introduce an equation system based on the combination of a cubic equation of state with appropriate mixing rules to predict the VLE without the need of binary interaction parameters fitted from experimental data.

Peng–Robinson [2] (PR) equation of state is one of the most popular cubic equations of state. It has been used extensively in process simulation tools to model the high-pressure VLE behavior. Among the commonly used mixing rules are Huron–Vidal [3] and Wong–Sandler [4]. Other mixing rules have been successfully used. A review on the available mixing rules is available elsewhere [5].

The objective of this work is to provide good estimates for binary interaction parameters to be used with the simplest and most widely-used equations system for the prediction of high-pressure vapor–liquid equilibrium. Thus, we estimate generalized values of the binary interaction parameters to be used with Peng–Robinson equation of state combined with van der Waals mixing rules. The work was limited to systems of hydrocarbons and related compounds.

The novelty of this work lies in the development of a general correlation for the binary interaction parameter of van der Waals mixing rules and the generation of the values of the adjustable parameters of the developed correlation that can be used to predict, with good accuracy, the vapor–liquid equilibrium of the studied systems.

The remainder of this paper is organized as follows. The next section introduces the Huron–Vidal and the van der Waals mixing rules as applied to the Peng–Robinson equation of state. The following section introduces the semi-empirical correlation that is developed in this work. Next, the methodology used to fit the experimental data and verify the correlation is presented. The following section presents the results of the work, discusses its significance and gives examples of the application of the newly-developed correlation to ternary systems. The last section ends with this work's conclusions.

Huron–Vidal and van der Waals mixing rules for the Peng–Robinson equation of state

In this and the following section, we present the theoretical basis for the proposed semi-empirical correlation. The thermodynamic properties and concepts used in this analysis follow the framework used in Orbey and Sandler [5]. The Peng–Robinson equation of state

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

can be used with the van der Waals mixing rules,

$$a = \sum_i \sum_j z_i z_j \sqrt{a_i a_j}(1-k_{ij}) \tag{2}$$

$$b = \sum_i x_i b_i \tag{3}$$

to predict the vapor–liquid equilibrium via the calculation of the fugacity coefficient of the liquid and the vapor phases according to

$$\ln\hat{\varphi}_i = \frac{b_i}{b}(Z-1) - \ln(Z-B) - \frac{A}{2\sqrt{2}B}\left(\frac{2\sum_j z_j a_{ij}}{a} - \frac{b_i}{b}\right)\ln\left[\frac{Z+(1+\sqrt{2})B}{Z+(1-\sqrt{2})B}\right] \tag{4}$$

where $B = bP/RT$, $A = aP/(RT)^2$, and $Z = PV/RT$. The fugacity coefficient is a measure of the deviation from the ideal-gas mixture behavior and is used in the phase equilibrium equation. The Huron–Vidal mixing rules use a different equation for the a parameter as follows:

$$a = b\left[\sum_i z_i \frac{a_i}{b_i} + \frac{G^{ex}_{\gamma}}{C^*}\right], \tag{5}$$

where $C^* = -0.62323$ for the Peng–Robinson equation of state. The resulting fugacity coefficient equation when using Huron–Vidal mixing rules becomes