

Evaluating the phase equilibria of liquid water + natural gas mixtures using cubic equations of state with asymmetric mixing rules

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ABSTRACT

Based on a previously developed liquid–liquid mixing rule we present a modified and robust mixing rule for accurate prediction of water content of natural gas mixtures and the natural gas solubility in liquid water phase. The non-density dependent mixing rule (NDD) and the new mixing rule are incorporated into the Peng–Robinson (PR), Soave–Redlich–Kwong (SRK), and Nasrifar–Bolland (NB) equations of state to investigate their accuracies in estimating the water content of the gas phase as well as the gas solubility in the aqueous phase. For each binary system water + hydrocarbon, water + carbon dioxide, water + hydrogen sulfide, and water + nitrogen, three binary interaction parameters are required to describe the gas–liquid water equilibria. In this work, experimental data from literature were used to tune the parameters. The results are in good agreement with experimental data, demonstrating the reliability of the new mixing rule and the thermodynamic approach used in this work.

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1. Introduction

Natural gas is generally saturated with water at reservoir conditions. Evaluating the water content of natural gas mixtures is important in a wide variety of applications in gas industry, e.g., for the design and optimization of operating conditions in gas pipelines and natural gas facilities. Additionally, presence of water in the gas phase may result in liquid water. The liquid water formed can damage equipments due to corrosion, two-phase flow and blockage during production and transportation. The water content of natural gas mixtures is reduced appreciably to avoid such problems. On the other hand, the solubility of hydrocarbons in water is important due to ecological concerns and new restrictions on the existence of organic pollutants in water streams. Therefore, it is of great interest to develop semi-empirical correlations, charts, or thermodynamic models for estimating the water content of natural gas mixtures and the gas solubility in the liquid water phase.

Several predictive models are available in the literature which can be used to calculate the phase equilibrium in natural gas + liquid water system. In general, these models include: (1) empirical or semi-empirical correlations and charts, (2) thermodynamic models which are based on equating the chemical potential or fugacity of each component in different phases.

There are various empirical or semi-empirical equations and charts with different accuracies for estimating the water content of gases, e.g., ideal model, ideal model + Poynting correction factor, Bukacek correlation [1], Sharma and Campbell method [2], Robinson et al. chart [3], Behr correlation [4], Maddox et al. correlation [5], Wichert and Wichert correlation [6], Kazim correlation [7], McKetta–Wehe chart [8], Ning et al. correlation [9], and Aqualibrium software [10]. In this paper, some of these methods are examined. These methods are simple and easy to use. Therefore, they have got a good popularity among the engineers in gas industry.

The validity test of the available correlations and charts to determine the water content of gases does not give complete satisfaction and their improvement is possible. These methods were generally developed with limited number of experimental data, mostly at high temperatures. In fact, during the methods development, the experimental data needed to describe the phase equilibria between water and hydrocarbon gases, and also between water and non-hydrocarbon gases were not available at low temperatures (typically lower than 298.15 K) [11]. Due to this deficiency, the calculated water content by the cited correlations and charts at low temperatures might not be accurate. Therefore, a simple and yet robust thermodynamic model which can be used for wide ranges of conditions is still necessary.

Thermodynamic models use different approaches to describe different phases. For example, some of them use activity coefficient and Henry's constant approach for modeling the liquid water phase; however, other models use the equation of state approach.

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It is likely to calculate the water content of hydrocarbons with reasonable accuracy using cubic equations of state (EoS) with a temperature-independent binary interaction parameter [12–14]. On the other hand, solubility of pure gases in water were investigated by many authors: Peng and Robinson [15,16], Mathias and Copeman [17], Kabadi and Danner [18], Michel et al. [19], Anderko [20], Victorov et al. [21], Yu and de Swan Arons [22], Soreide and Whitson [23], Daridon et al. [24], Apostolou et al. [25], and Nasrifar and Moshfeghian [26]. Due to the inability of EoS/mixing rules to represent the hydrophobic effect in the aqueous phase, the prediction of hydrocarbons solubility in water is poor. To overcome this deficiency, on the basis of experimental evidence, empirical mixing rules for the attractive energy parameter of cubic EoS were developed by Kabadi and Danner [18], Michel et al. [19] and Nasrifar and Moshfeghian [26]. The Michel et al. [19] mixing rule illustrates improvement over the Kabadi and Danner [18] mixing rule. The Nasrifar and Moshfeghian mixing rule [26] also illustrates improvement over Michel et al. [19], and Kabadi and Danner [18] models. Nasrifar and Moshfeghian [26] developed a mixing rule that seems to be accurate in prediction of heavy and cyclic hydrocarbon solubility in water for a wide temperature range.

The aim of the present work is developing an asymmetric mixing rule based on the Nasrifar and Moshfeghian (NM) mixing rule [26] for the attractive energy parameter of cubic EoS. This mixing rule is used to predict the phase equilibria in natural gas + liquid water systems for a wide range of temperature. For this purpose the water content data of natural gas main components as well as natural gas components solubility in water-rich phase for some binary and multicomponent systems were collected from the literature. Three cubic EoS were used for calculations, i.e., the Peng–Robinson (PR) EoS [27], the Soave–Redlich–Kwong (SRK) EoS [28] and the Nasrifar–Bolland (NB) EoS [29]. Considering the simplicity and wide applications of the cubic EoS, it would be desirable to calculate the phase equilibria in natural gas main components + liquid water systems.

2. Thermodynamic model

2.1. Model

For calculating the gas–liquid equilibria of natural gas + liquid water systems, three cubic EOS are used. These EoS comprise the PR EoS [27], the SRK EoS [28] and the NB EoS [29]. A two-parameter cubic equation of state can generally be expressed by

$$P = \frac{RT}{v-b} - \frac{a}{(v+ub)(v+wb)} \quad (1)$$

where P , T , v and R are the pressure, temperature, molar volume and universal gas constant, respectively. The u and w are equation of state dependent constants. For the PR EoS, $u = -0.4142$, $w = 2.4141$; for the SRK equation, $u = 0$, $w = 1$; and for the NB EoS, $u = w = 1/\sqrt{3}$. For these three EoS, the b -parameter is expressed by

$$b = \sum_i x_i b_i \quad (2)$$

For polar–non-polar interactions, however, the classical van der Waals mixing rule for the attractive parameter a is not satisfactory and an unconventional form of the classical mixing rule is required.

2.2. The new mixing rule for the attractive parameter

In systems which contain water, the asymmetric interaction cannot efficiently be accounted for by the classical mixing rule. To overcome this deficiency several authors, e.g., Mathias and Copeman [17], Kabadi and Danner [18] and Michel et al. [19] presented

unconventional mixing rules for the attractive energy parameter of the cubic EoS. Kabadi and Danner [18] developed a non-quadratic mixing rule, considering the hydrophobic interactions between water and hydrocarbons in water-rich phase. The mixing rule is expressed by

$$a = x_1^2 a_{11} f(x_2) + x_2^2 a_{22} + 2x_1 x_2 (a_{11} a_{22})^{1/2} (1 - k_{12}) \quad (3)$$

$$f(x_2) = 1 + 2 \frac{G(1 - T_{r,1}^{0.8})}{a_{11}} x_2 \quad (4)$$

where G is a constant and $T_{r,1} = T/T_{C,1}$. In Eqs. (3) and (4) and those that follow the subscript 1 stands for water.

Later, Michel et al. (MHP) [19] proposed

$$f(x_2) = 1 + \beta_{12} x_2 \exp(-\alpha x_2) \quad (5)$$

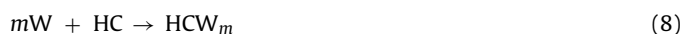
where $\alpha = 10$ and β_{12} is a function of temperature according to

$$\beta_{12} = \tau T^n \quad (6)$$

Nasrifar and Moshfeghian [26] defined a parameter Φ which corrects the water–water interaction in the presence of hydrocarbons. This parameter accounts for the changes in the structure of water due to the presence of hydrocarbons. In fact, some of water molecules are separated from the water structure, producing free space or holes which can be occupied by the hydrocarbon molecules [31]. Nasrifar and Moshfeghian [26] presented the following equation for considering water–water interactions between water molecules in the structural body and free water molecules

$$\Phi = \frac{a'_{11}}{a_{11}} \quad (7)$$

where a_{11} is the water–water interaction in the absence of hydrocarbon and a'_{11} in the presence of hydrocarbon. Nasrifar and Moshfeghian [26] constructed a quasi-chemical reaction between m water molecules and a hydrocarbon molecule to produce a complex as follows



with

$$K_E = \frac{X_{HCW_m}}{X_1^m X_2} \quad (9)$$

where K_E is an equilibrium constant and X the true mole fraction. Taking it for granted that the complex is responsible for the changes in the water–water interaction, Nasrifar and Moshfeghian [26] obtained the following relation for the parameter Φ that seems to be adequate for correlating the liquid–liquid equilibria of water–hydrocarbon systems for a wide range of temperature

$$\Phi = 1 + \delta_{12} x_1^2 x_2 \quad (10)$$

with

$$\delta_{12} = \left(m_1 + \frac{m_2}{T} \right) \exp \left(-\frac{\Delta H^\circ}{RT} \right) \quad (11)$$

Considering water–water interaction in the presence of hydrocarbons, one can use the van der Waals' mixing rule in the following form

$$a = x_1^2 a'_{11} + x_2^2 a_{22} + 2x_1 x_2 (a_{11} a_{22})^{1/2} (1 - k_{12}) \quad (12)$$

Combining Eqs. (7) and (12) yields

$$a = x_1^2 a_{11} \Phi + x_2^2 a_{22} + 2x_1 x_2 (a_{11} a_{22})^{1/2} (1 - k_{12}) \quad (13)$$

Eq. (13) together with Eqs. (10) and (11) complete our relationship, namely the NM mixing rule. Nasrifar and Moshfeghian [26] evaluation for the compositional dependence of Φ shows that the function provides a maximum at $x_2 = 0.1$ and approaches unity as $x_2 \rightarrow 0$, and $x_2 \rightarrow 1$. For the case $x_2 \geq 0.6$, i.e., for the gas phase at

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