



Thermodynamic modeling of saturated liquid compositions and densities for asymmetric binary systems composed of carbon dioxide, alkanes and alkanols



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ABSTRACT

The present study mainly focuses on the phase behavior modeling of asymmetric binary mixtures. Capability of different mixing rules and volume shift in the prediction of solubility and saturated liquid density has been investigated. Different binary systems of (alkane + alkanol), (alkane + alkane), (carbon dioxide + alkanol), and (carbon dioxide + alkane) are considered. The composition and the density of saturated liquid phase at equilibrium condition are the properties of interest. Considering composition and saturated liquid density of different binary systems, three main objectives are investigated. First, three different mixing rules (one-parameter, two parameters and Wong–Sandler) coupled with Peng–Robinson equation of state were used to predict the equilibrium properties. The Wong–Sandler mixing rule was utilized with the non-random two-liquid (NRTL) model. Binary interaction coefficients and NRTL model parameters were optimized using the Levenberg–Marquardt algorithm. Second, to improve the density prediction, the volume translation technique was applied. Finally, Two different approaches were considered to tune the equation of state; regression of experimental equilibrium compositions and densities separately and spontaneously. The modeling results show that there is no superior mixing rule which can predict the equilibrium properties for different systems. Two-parameter and Wong–Sandler mixing rule show promoting results compared to one-parameter mixing rule. Wong–Sandler mixing rule in spite of its improvement in the prediction of saturated liquid compositions is unable to predict the liquid densities with sufficient accuracy.

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1. Introduction

The design and development of many chemical and petroleum processes, such as separation and upgrading of petroleum products, as well as enhanced oil recovery techniques require accurate prediction of phase equilibria and mutual solubility of light gases in heavy hydrocarbons and alcohols [1]. Experimental measurements, molecular simulation, empirical correlations, and equation of state (EOS) modeling are different approaches to obtain the phase equilibrium information. Experiments in spite of their accuracy are expensive and time-consuming; thus, it is not feasible to obtain the experimental data for all mixture over wide ranges of pressures and temperatures. Molecular simulation is a theoretical approach hindered by high computational complexity. Depending on the system under study, the execution time is a function of the molecular size and structure. This issue makes the molecular

simulation impractical for chemical and petroleum industries. The empirical correlations are commonly developed on the basis of experimental data and are only applicable for a specified system over a limited range of conditions.

EOSs are the most popular approach for the phase behavior study. In addition to being fast, this approach needs a limited number of parameters as input. EOSs can be used to regenerate the phase equilibrium data, predict the volumetric properties of substances, and describe (vapor + liquid) equilibrium [2]. After van der Waals EOS [3] in 1873, Redlich and Kwong [4] proposed their EOS with two parameters in 1949. The proposed EOS can predict the properties of components with sufficient accuracy, but the (vapor + liquid) equilibrium prediction were relatively poor [5]. In 1972, Soave [5] presented a modification to Redlich–Kwong EOS and suggested a temperature dependent parameter to improve the calculation of saturated pressure for pure substances. The modified EOS, in spite of its strength faced some weaknesses; failure to predict liquid densities was one of its main problems. In fact, it always predicts specific volumes greater than the experimental values [6]. Peng and Robinson proposed an EOS to improve the

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predictions of the liquid densities and vapor pressures [6]. Peng–Robinson (PR) EOS, despite its weaknesses such as inaccurate prediction around the critical point, is very common.

Employing the mixing rules, makes EOSs a powerful tool for phase behavior modeling of mixtures. Mixing rules are used to calculate the EOS input parameters for mixtures. In 1873, van der Waals [3] introduced classical mixing rule which widely is used for calculation of mixture parameters. Han *et al.* [7] showed this mixing rule is capable of phase behavior modeling of non-polar or slightly polar molecules. In spite of its strength, this mixing rule shows weakness in the prediction of polar components' properties [8]. In 1992, Wong and Sandler [9] developed a mixing rule based on equivalences of excess Helmholtz energy of an EOS with an activity coefficient model at infinite pressure. Wong–Sandler mixing rule was successful in the prediction of (polar + nonpolar) systems. Voros *et al.* [10] compared the results of EOS coupled with one-parameter, two-parameter, and Wong–Sandler mixing rules. They indicated temperature and pressure dependent binary interaction coefficients can predict the phase behavior with higher accuracy. One-parameter and two-parameter mixing rules showed convergence problems in the vicinity of the critical point.

Orbey and Sandler [11] tested Wong–Sandler mixing rule for binary systems containing long chain hydrocarbon, polymer, and conventional solvents. They modeled solvent partial pressure in concentrated polymer and vapor phase concentration for (polymer + conventional solvent) and (solvent + hydrocarbons) systems. Wong–Sandler mixing rule was the best which can describe their systems' behavior. Using this mixing rule for phase behavior study has become popular recently. Lopez *et al.* [12] used Wong–Sandler mixing rule to predict carbon dioxide fraction in *n*-alkanols. Elizalde *et al.* [13] used Wong–Sandler mixing rule to model bubble point pressure and carbon dioxide vapor phase fraction for asymmetric binary mixtures of (carbon dioxide and *n*-alkanols). Foster *et al.* [14] used two-parameter mixing rule for the prediction of bubble point pressure and vapor phase fraction of the same systems. In a subsequent study, Elizalde *et al.* [15] used Wong–Sandler mixing rule to predict the phase behavior of (carbon dioxide + 1-butanol) and (carbon dioxide + 2-butanol) systems. They used two approaches to obtain the adjustable parameters; using bubble point pressure and vapor liquid fraction, and using liquid and vapor densities as properties of interest. None of the above efforts investigate liquid mole fraction and liquid density simultaneously as the objective function.

This research is a continuing part of our previous works [16–24] for experimental and modeling study of hydrocarbon and non-hydrocarbon systems. The experimental data from our previous studies have been used to conduct a comprehensive EOS modeling of binary polar and non-polar systems by utilizing one-parameter, two-parameter, and Wong–Sandler mixing rule. The volume translation technique is also used to improve volumetric behavior prediction. The binary systems of (methane + methanol, ethanol, and 1-propanol), (methane + *n*-tetradecane and *n*-octadecane), (ethane + *n*-tetradecane and *n*-octadecane), (carbon dioxide + methanol, ethanol, and 1-propanol), and (carbon dioxide + *n*-decane, *n*-tetradecane, and *n*-octadecane) are of interest. The Levenberg–Marquardt algorithm was used to optimize the interaction coefficients and volume shifts parameters in order to predict saturated liquid compositions and densities.

2. Modeling and methodology

2.1. Equation of state

The PR EOS [6] was used to predict the experimental data of saturated liquid compositions and densities. Due to its relative simplicity and accuracy for the phase behavior of petrochemical

products, this EOS has been widely used by the chemical and petroleum industries. The PR EOS is presented as,

$$P = \frac{RT}{v_M - b} - \frac{a(T)}{v_M(v_M + b) + b(v_M - b)}, \quad (1)$$

where P is the absolute pressure, T is the absolute temperature, V_M is molar volume, and R is the ideal gas constant. The attraction and repulsion molar volume parameters, a and b , are calculated as,

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

$$b = 0.07780 \frac{RT_c}{P_c}, \quad (3)$$

where subscript c corresponds to the critical point. The attractive term in Eq. (2) is calculated by

$$\alpha(T)^{1/2} = 1 + k(1 - T_r^{1/2}), \quad (4)$$

$$k = 0.37464 + 1.54226\omega - 0.26992\omega^2, \quad (5)$$

where ω is the acentric factor and T_r represents reduced temperature, which is calculated as T/T_c . As equations (2)–(5) show the attraction and repulsion terms depend on the component properties. The attraction and repulsion parameters for mixtures are obtained using mixing rules. Three different mixing rules of one-parameter classical, two-parameter classical, and Wong–Sandler were considered in this study.

2.1.1. One-parameter classical mixing rule

This is the first and the most popular mixing rule which has been used for the phase behavior modeling of the mixtures. The simplicity of this mixing rule sacrifices its accuracy for the modeling of the complex and polar systems. The one-parameter classical mixing rule is

$$a_m = \sum_i \sum_j x_i x_j a_{ij}, \quad (6)$$

$$b_m = \sum_j x_j b_j, \quad (7)$$

x_i is the mole fraction of component i in the gas and liquid phase. The parameter b is obtained by the average molecular volume, which is based on arbitrary assumptions and is a mathematically simple formula (equation (3)) [25]. In the systems containing molecules with similar sizes in moderate densities, the mixing rule for parameter b does not have significant effect on the EOS results; however, the parameter a considerably can change the fugacities [25]. The parameter a reflects the attraction strength and is related to pure components attraction parameter by,

$$a_{ij} = \sqrt{(a_i a_j)(1 - k_{ij})}, \quad (8)$$

where k_{ij} is the interaction coefficient for the binary pairs within the mixture and $k_{ij} = k_{ji}$. Equation (8) is called the geometric mean assumption and was proposed by Berthelot [25]. The one-parameter mixing rule depends on only one binary interaction coefficient; thus, it cannot give accurate predictions near critical regions or for systems containing polar components or complex structured molecules. The equivalence of the fugacity for each component in each phase is the criteria for equilibrium. The general equation for the fugacity coefficient calculation using one-parameter mixing rule is,

$$\ln \varphi_i = -\ln(z - B) + (Z - 1)B'_j - \frac{A}{2\sqrt{2}B}(A'_j - B'_j) \times \ln \left[\frac{z + (\sqrt{2} + 1)B}{z - (\sqrt{2} - 1)B} \right], \quad (9)$$

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