



Recent advances in modeling the vapor-liquid equilibrium of mixed working fluids



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ABSTRACT

Vapor-liquid equilibrium (VLE) properties of mixed working fluids are essential for the study of organic fluids for thermodynamic cycles such as heat pumps or organic Rankine cycles. Thus, the typical and recent models for the VLE calculation of mixed working fluids are reviewed in this paper. The most popular cubic equations of state (EOSs) and two mixing rules, namely the Van der Waals and the excess free energy, are summarized, respectively. VLE data of 13 alternative working fluids at different temperatures are employed to exhibit the capacities and limitations of three predictive models. The calculated VLE results show that the model with Van der Waals mixing rules is only valid for some types of mixture, while the accuracy of the model with excess free energy mixing rules is greatly influenced by the UNIFAC group parameters, which are usually fitted from the VLE data instead of the activity coefficient data. Thus, a generalized model for mixed working fluids should be derived from the molecular theory or the group contribution method, in which the group parameters are fitted from the large VLE data.

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1. Introduction

Organic working fluids have been widely used in several application domains, such as refrigeration, heat pump and organic Rankine cycle. The physical properties of working fluids directly determine the thermodynamic efficiency of system, the design of system components, the stability and safety of system. Thus, a high-efficient, safe and economical operation of thermodynamic cycle is highly dependent on working fluids with appropriate properties. In addition to the thermodynamic properties of working fluids, environmental properties, such as ozone depletion potential (ODP) and global warming potential (GWP), have to be considered in the screening of working fluids with growing concerns regarding the depletion of the ozone layer and the greenhouse effect [1]. Recently, due to high ODP and high GWP, the traditional organic working fluids chlorofluorocarbon (CFC) have been phased out in accordance with the protocol of Montreal and the hydrochlorofluorocarbon (HCFC) will also be phased out in 2040. Therefore, it's urgent to search the high-efficient fluids which are friendly to the environment.

Although many researchers have proposed suitable pure fluids for different applications, few pure fluids, which are free of all environmental and safety concerns, chemically and thermally stable, and perform efficiently, have been found [2–4]. Thus, mixtures, whose individual drawbacks of the components can be compensated by each other, are recommended as candidates of working fluids. Basically, the mixed working fluids are preferable to pure working fluids on account of energy saving and the flexibility of operation [5–7].

A reliable thermodynamic model is required for evaluating the performance of a given mixture in a thermodynamic cycle. In general, the experimental data of vapor-liquid equilibrium (VLE) for mixed working fluids are used to establish the highly accurate Helmholtz energy equation, which is widely applied to calculate the thermodynamic properties of corresponding mixture [8]. Furthermore, accurate VLE data are essential for designing and modeling thermodynamic processes, which include the evaporation and condensation of working fluids, the constituent separation of mixtures [9]. For the mixed working fluids being in VLE, they may produce different types of phase behavior, because of the different molecular interactions and phase conditions. Although experiments can provide accurate data at specific phase conditions for mixtures, such data are limited and can't be expected to meet the expanding industrial needs for thermodynamic design and

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development [10]. Besides, given a huge number of mixed working fluids, it's impossible to provide VLE information for every mixture by the time-consuming phase equilibrium experiment with high costs. Therefore, many VLE models have been proposed to provide predictions of VLE for a wide variety of mixtures exhibiting varied phase behaviors, based on the limited experimental data [11–14].

Such calculation models can be categorized into two approaches. The first approach utilizes an equation of state (EOS) to describe the phase behavior for both the liquid and vapor phases. The second approach utilizes an activity coefficient model to describe the liquid phase, while a different model, usually an EOS, is used to describe the vapor phase [10]. Existing studies have demonstrated that the EOS model can be successfully applied to correlate the VLE data of mixed working fluids over broad ranges of temperature and pressure [15–18]. In contrast, the activity coefficient model has been applied successfully at low temperatures where the liquid phase is relatively incompressible. However, this model is deficient in describing the phase behavior at high pressures [10,15]. Thus, for the above reasons, this paper is focused on the EOS model.

For the EOS model, cubic EOSs, such as Soave–Redlich–Kwong (SRK) and Peng–Robinson (PR), are widely used to predict the VLE of mixed working fluids, due to their inherent simplicity and efficiency [15]. A compositional dependence has to be introduced to account for the molecular interactions in mixtures, in order to predict the phase behavior using cubic EOSs. All extensions of cubic EOSs to mixtures are, at least partially, empirical in nature, because there is no exact statistical mechanical solution relating the properties of dense fluids to their intermolecular potentials, and the detailed information on such intermolecular potentials is unavailable [19]. Therefore, a variety of mixing rules have been proposed to determine the parameters of cubic EOS for mixtures over the years [15,19]. Generally speaking, the proposed mixing rules can be classified into two categories, namely, Van der Waals (VDW) mixing rules and excess free energy (G^E) mixing rules. The VDW mixing rules have been used to describe the VLE of mixed working fluids for decades, because of their simplification and relative accuracy for many mixture systems [20–22]. A route for developing excess free energy mixing rules is to combine a cubic EOS with an activity coefficient model, often a local composition model like Wilson, NRTL, UNIQUAC or UNIFAC [12,23–25]. The excess free energy mixing rules have enhanced dramatically the range of cubic EOS's applicability and can give a good prediction for high pressure VLE of mixtures. Furthermore, the group contribution activity coefficient model UNIFAC has been widely used to develop completely predictive models for mixed working fluids [25].

The models, which can be utilized to predict the VLE of mixtures, usually consist of two parts including cubic EOSs and mixing rules. This paper presents a state-of-the-art review of these models and discusses the capabilities and limitations of three predictive models in exhibiting the phase behaviors of mixed working fluids. The methodology of VLE is presented to demonstrate the process of VLE calculations in the next section. In Section 3, commonly-used cubic EOSs are summarized and discussed. Two mixing rules involved the van der Waals and the excess free energy are reviewed respectively in Section 4. In Section 5, the performances of three completely predictive models in predicting the VLE of mixed working fluids are discussed by comparing the calculated results with the experimental data. The knowledge gaps and development directions of VLE models are presented in Section 6. Conclusions of this review on modeling the VLE of mixtures are given in Section 7.

2. Methodology of VLE

For the mixture being in VLE, the required thermodynamic

condition is that the temperature, pressure and fugacity of each species should be the same in liquid and vapor phases [15]. That is,

$$T_i^L = T_i^V = T \quad (1)$$

$$P_i^L = P_i^V = P \quad (2)$$

$$f_i^L(T, P, z_i) = f_i^V(T, P, y_i) \quad (3)$$

Where superscripts L and V represent liquid and vapor, respectively. z_i, y_i sequentially denote the molar fraction of species i in the liquid and vapor phases. The key of VLE calculation is to express the fugacity as a function of temperature, pressure and composition. An EOS is generally used to obtain the fugacity of species i in the vapor phase, and the generalized form is

$$\ln \left(\frac{f_i^V(T, P, y_i)}{y_i P} \right) = \frac{1}{RT} \int_V^\infty \left[\left(\frac{\partial(PV/RT)}{\partial N_i} \right)_{T, V, N_{j \neq i}} - 1 \right] \frac{dV}{V} - \ln Z^V \quad (4)$$

Where V is the total volume, Z^V is the vapor compressibility factor computed from the EOS. However, there are two different methods to describe the liquid phase: either the same EOS used for the vapor phase is also used for the liquid phase or the activity coefficient method is employed.

For the activity coefficient method, the fugacity of species i in the liquid phase is obtained by

$$f_i^L(T, P, z_i) = z_i \gamma_i f_i^{PL}(T, P) \quad (5)$$

Where $f_i^L(T, P)$ is the fugacity of pure component i as a liquid at the temperature and pressure of the mixture, and can be calculated from EOSs. At low temperature and pressure, $f_i^L(T, P)$ is approximately equal to the vapor pressure of pure component. For the activity coefficient γ_i , many local composition models, such as UNIFAC, NRTL and Wilson, have been proposed to relate γ_i to composition z_i [19]. However, these models are only valid at low pressure and temperature where the liquid phase is relatively incompressible. By contrast, the EOS model can be applied to the liquid phase over a wide range of temperatures and pressures. With the same EOS used for the vapor phase, the fugacity of a species in a liquid mixture is computed from

$$\ln \left(\frac{f_i^L(T, P, z_i)}{z_i P} \right) = \frac{1}{RT} \int_V^\infty \left[\left(\frac{\partial(PV/RT)}{\partial N_i} \right)_{T, V, N_{j \neq i}} - 1 \right] \frac{dV}{V} - \ln Z^L \quad (6)$$

Where the liquid compressibility factor Z^L is derived from the EOS. This equation differs from Eq. (4) only in that the smallest volume, which is the liquid phase solution to the EOS, is used to calculate the fugacity. Due to the applicability of Eq. (6) over a wide range of temperatures and pressures in calculating the liquid fugacity, the EOS model has been extensively used to predict the VLE of mixed working fluids.

Numerous EOSs have been proposed to establish the pressure-volume-temperature relationship of organic fluids. In general, these proposed EOSs can be categorized into the “analytical” and “non-analytic” types [15]. The former means that when T and P are specified, V can be found analytically. This type of EOSs is represented by the cubic EOSs, such as SRK and PR. However, V is calculated numerically in the latter approach. In order to describe the complexity of property behavior, a large number of fitted

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