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Investigation on vapor liquid equilibrium for strongly-zeotropic ternary mixture of 2,3,3,3-tetrafluoroprop-1-ene (R1234yf) + trifluoromethane (R23) + tetrafluoromethane (R14)

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ABSTRACT

The cubic equation of state/excess Gibbs free energy (CEoS/G^E) model is a new idea to predict non-ideal systems. In this study, the Peng-Robinson (PR) EoS combined with the Wong-Sandler (WS) mixing rule and the modified UNIFAC group contribution activity model was used to calculate the vapor liquid equilibrium (VLE) data. The average absolute relative deviations (AARD) of pressure and the average absolute deviations (AAD) of the vapor phase mass fraction between the calculated results and experimental data are 0.87% and 0.005 for fluoroethane (R161) + 2,3,3,3-tetrafluoroprop-1-ene (R1234yf) over the temperature range of (283.15–323.15 K) and at pressures varying from 0.4 MPa to 1.8 MPa, respectively. The liquid and vapor phase mass fraction deviations are within ±0.028 and ±0.025 for difluoromethane (R32) + pentafluoroethane (R125) + 1,1,1,2-tetrafluoroethane (R134a) system at temperatures of (205–350 K), respectively. The VLE behavior for the strongly-zeotropic mixture of 2,3,3,3-tetrafluoroprop-1-ene (R1234yf) + trifluoromethane (R23) + tetrafluoromethane (R14) which is suitable for the three-stage auto cascade refrigeration system was calculated at pressures of (0.2–2.2 MPa) and the corresponding three-dimensional phase diagrams were constructed. It was found that the sliding temperature increases with the decrease of pressure and the maximum predicted sliding temperature reached 73 K.

1. Introduction

In recent years, with the rapid development of high-tech fields in energy, medical, and military sectors and in the biological sciences and other life sciences, the demand and requirement for low temperature and super-low temperature applications have increased. Single stage vapor compression refrigerators are widely used for providing temperatures warmer than 233 K. Temperatures lower than 233 K would require expanding the refrigerant to pressures less than 1 bar, resulting in low volumetric efficiency of compressors, possibility of atmospheric air leaking into the system, and high compressor discharge temperatures that can result in the dissociation of the compressor lubricating oil [1]. The auto-cascade refrigeration system uses mixed refrigerants to achieve multilevel cascade through one compressor, which can obtain a low temperature below 233 K and therefore greatly simplify the system [2]. Typically, the more stages an auto-cascade refrigeration system has, the lower temperature it could obtain. For example, a two-stage auto-cascade system can be utilized to achieve temperatures of approximately 203 K, and the lower temperature of 173 K can be reached using a three-stage auto-cascade refrigeration system [3]. Fuderer [4] proposed a new type of auto-cascade refrigeration cycle utilizing gas-liquid separations with different mixtures. With this system, evaporation temperatures of 160 K and 117 K were obtained, respectively. Missimer [5,6] further examined an auto-cascade refrigeration system with bypass regulation that was based on the research of Fuderer [4]. This system addressed issues with high exhaust pressures, stability, and control. Luo et al. [7] successfully obtained a super-low temperature of 51.2 K using an open-type auto-cascade system with a ternary mixture; thus far, this is the lowest temperature achievable using zeotropic J-T refrigerant mixtures. Xiao et al. [8] used a four-stage auto-cascade system with an isobutene (R600a) + trifluoromethane (R23) + tetrafluoromethane (R14) + argon(R740) mixture at a mass fraction of 45 + 21 + 19 + 15 to increase the cooling capacity to 100 W at the temperature of 123 K. An efficient auto cascade refrigeration system requires a careful balance between the refrigerant mixture and the system flow pattern and hardware. Many scholars have noted that high numbers of stages of the auto-cascade system overcomplicate the operation of the refrigeration equipment. However, two- or three-stage

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auto-cascade cycles are unable to meet the low temperature requirements or coefficients of performance (COPs) of refrigeration systems. Mixtures with large temperature glides can accommodate low temperature and COP requirements well. However, these mixtures typically need more stringent control. Therefore, thermodynamics properties and vapor liquid equilibrium (VLE) characteristics of mixtures play crucial roles in the design and improvement of auto-cascade refrigeration systems, especially in optimizing the separation of mixed refrigerants in vapor-liquid separators.

To design a refrigeration system appropriately using mixed refrigerants, a large amount of VLE data is required. Through experimentation, VLE data can be obtained. However, significant portions of data cannot be experimentally obtained and the molecular modelling with sufficient accuracy is a reliable and robust route to VLE of mixtures. Many experiments on azeotropic and zeotropic mixed refrigerants have recorded the VLE data of binary and ternary mixtures. Huang et al. [9] predicted ternary VLE for 33 systems using molecular simulations. Diefenbacher et al. [10] examined the binary mixtures of CO_2, CH_2F_2, CHF_3, and SF_6. Williams-Wynn et al. [11,12] obtained binary VLE data for CO_2 + n-hexane and trifluoromethane + n-hexane with static-analytic and static-synthetic phase equilibrium measurements and showed that the utilized thermodynamic model (Peng–Robinson equation of state with the Mathias–Copeman alpha function, coupled with the Wong–Sandler mixing rules) correlated well with experimental data. Alvarez et al. [13,14] examined the vapor-liquid equilibrium of binary systems, i.e., an ionic liquid and a supercritical fluid (CO_2 and CHF_3) and an ionic liquid and hydrocarbons using the Peng–Robinson equation of state (PR-EoS). These researchers further showed that the Wong-Sandler (WS) mixing rules better represented the data, with both activity coefficient models showing high accuracy. Hu et al. conducted experiments and simulations for systems used at ambient temperatures, including the binary and ternary mixtures of 2,3,3,3-tetrafluoroprop-1-ene (R1234yf) + 1,1-difluoroethane(152a) [15], CO_2 + 2,3,3,3-tetrafluoroprop-1-ene (R1234yf) [16], 1,1,1,2-tetrafluoroethane (R134a) + 1,1,1,2,3,3,3-heptafluoropropane (R227ea) and 1,1,1-trifluoroethane(R143a) + 2,3,3,3-tetrafluoroprop-1-ene (R1234yf) [17], and 2,3,3,3-tetrafluoroprop-1-ene (R1234yf) + 1,1,1,2-tetrafluoroethane (R134a) + isobutene (R600a) [18]. Zhang et al. [19] and Guo et al. [20] studied the VLE characteristics of cryogenic mixed refrigerants, such as the mixtures of N_2 (R728) + methane (R50), N_2 (R728) + tetrafluoromethane (R14) and N_2 (R728) + methane (R50) + ethane (R170) [21]. Zhu [22] investigated the VLE properties of methane (R50) + tetrafluoromethane (R14) + ethane (R170) at cryogenic temperatures and found that R50 + R170 and R14 + R170 had properties characteristic of liquid-solid equilibrium. These researchers also investigated the interaction coefficient k_{ij} and the vapor-liquid-liquid and liquid-solid equilibrium. These studies have produced a large set of reliable phase equilibrium data and have also provided direction for additional studies. Gao et al. [23] presented an improved lattice Boltzmann (LB) method to simulate solid-liquid phase change with natural convection in porous media under local thermal non-equilibrium (LTNE) conditions and pointed that the present model could be more accurate than the previous model (single relaxation time (SRT) model of Ref. [42]). However, while a broad range of VLE was examined, most of the studies concentrated on near-azeotropic mixed refrigerants. Few reports have considered the VLE of R1234yf + R23 + R14, a ternary mixture with a large temperature glide, which can achieve a 150 K temperature in a three-stage auto-cascade refrigeration system.

Based on the results of our previous work [24], we present the thermodynamics properties of the R161 + R1234yf and R32 + R125 + R134a system calculated based on certain mass fractions by the PR-EoS [25] combined with the WS [26] mixing rule and the modified UNIFAC (M-UNIFAC-PSRK) [27,28] developed in the predictive Soave–Redlich–Kwong (PSRK) group contribution equation of state, which is a well-established method for the prediction of thermodynamic properties required in process simulation [29]. We calculated the dew point, bubble point, and the vapor and liquid mass fractions at constant temperature and pressure. Furthermore, we showed ways to ascertain the state of the mixture based on temperature, pressure and component concentrations. The accuracy of the model was verified by comparing with the corresponding experimental data in related literature [30,31]. Thus, the strongly, zeotropic ternary R1234yf + R23 + R14 mixture in a three-stage auto-cascade refrigeration system was modeled, and the corresponding three-dimensional phase equilibrium diagrams were estimated. The proposed model provides reliable phase equilibrium data and can be used as a guide or reference for optimizing the separation of the mixtures and the design of refrigeration systems.

2. The thermodynamic framework

2.1. Model selection

EoS method and activity coefficient method ($\gamma - \varphi$) are the common approaches for calculating the VLE data. The most elementary thermodynamics parameter of a fluid medium is the relationship between pressure, volume and temperature (*pvT*). Because the EoS is the embodiment of the *pvT* property of a fluid medium, the thermodynamics properties of the fluid medium can be attributed to the EoS. It is necessary to introduce the component variable according to the characteristic of mixtures when the EoS is extended to the mixtures, and the calculation precision will be improved obviously. However, according to different systems and EoS, different mixing rules need to be combined, and the accuracy is not particularly high when predicting the non-ideal system. It is necessary for $\gamma - \varphi$ method to combine the calculation of activity coefficients with fugacity coefficients to predict phase equilibrium, and to determine the reference states of pure substance as well. Furthermore, both of EoS and $\gamma - \varphi$ could not accurately describe the near-critical state and the critical state [32].

Thus, using the suitable mixing rules may combine the advantages of these two approaches. This combined method, namely the $CEoS/G^E$ approach, may effectively predict the complicated phase behavior of the mixture systems. With an EoS even supercritical components can be considered and other thermodynamic quantities like densities or enthalpies can be obtained directly, which are required as additional information in the $\gamma - \varphi$ approach. The WS mixing rule combined with the two parameter cubic EoS, is applicable to the calculation of phase equilibrium of high pressure and low pressure, polar and non-polar systems. Therefore, it has excellent temperature and pressure extrapolation properties. Chen et al. [28] proposed a modified group contribution method (M-UNIFAC-PSRK) used in the PSRK to calculate the mixture parameter *a*. This paper presented the called PR-WS-UNIFAC-PSRK model which is based on the PR EoS combined with the WS mixing rule and the M-UNIFAC-PSRK group contribution method. The VLE behavior of many binary and ternary mixtures was calculated.

2.2. Modelling details

The Critical properties, normal boiling point and acentric factors of pure components listed in Table 1 (from the National Institute of Standards and Technology (NIST) database) were