Isothermal vapor−liquid equilibria measurements for binary systems of 2,3,3,3-tetrafluoropropene (HFO-1234yf) + 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) and 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) + 2-chloro-1,1,1,2-tetrafluoropropane (HCFC-244bb)

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ABSTRACT

This paper presents the measurements of isothermal vapor-Liquid equilibria (VLE) data for two binary systems of 2,3,3,3-tetrafluoropropene (HFO-1234yf) + 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) and 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf) + 2-chloro-1,1,1,2-tetrafluoropropane (HCFC-244bb). The measurements were performed with an apparatus based on the static-analysis method. The HFO-1234yf + HCFO-1233xf system was measured at three temperatures from (293.15 to 313.15) K, and the HCFO-1233xf + HCFC-244bb system was measured at three temperatures from (303.15 to 323.15) K. The system of HFO-1234yf + HCFO-1233xf shows a small deviation from Raoult's law and dose not exhibit azeotropic behavior, while the system of HCFO-1233xf + HCFC-244bb exhibits near azeotropic behavior within the complete range of composition. All of the experimental data were correlated with the Peng−Robinson equations of state with the van der Waals mixing rules. Good consistency was obtained between the experimental data and correlated values for the both systems in the experimental temperature range. Thermodynamic consistency testing was also performed by the data-reduction method for the observed experimental data.

1. Introduction

The F-gas regulations have specified that the refrigerants with a global warming potential (GWP) greater than 150 were banned from use in the new automotive air conditioners in the European Union since 2011 and will be absolutely forbidden in all cars in 2017 [1]. Regarding this requirement, 2,3,3,3-tetrafluoropropene (HFO-1234yf) is expected as the strongest alternative candidate for current refrigerant 1,1,1,2-tetrafluoroethane (R-134a), because it has excellent environment parameters with GWP of 4 and ozone depleting potential (ODP) of 0 [2], and it also exhibits similar thermodynamic properties to R-134a [3]. Furthermore, this refrigerant offers unique properties such as low toxicity, low flammability, and stable chemical nature [4]. Recently, automobile manufacturers have considered HFO-1234yf as a 'drop-in' solution to replace of R-134a refrigerant [5].

For the production of HFO-1234yf, regardless of various synthetic routes, 2-chloro-3,3,3-trifluoropropene (HCFC-1233xf) and 2-chloro-1,1,1,2-tetrafluoropropane (HCFC-244bb) are usually used as raw materials/intermediates to synthesize HFO-1234yf [6–10]. The separation of mixtures containing above intermediates and product plays an extremely important role in the purification process of HFO-1234yf. Vapor liquid equilibrium (VLE) data is the fundamental thermodynamics property which facilitates the design of separation processes. Moreover, accurate experimental VLE data provide the basis necessary to develop commercial technique. Therefore, the VLE data are strongly desired for the separation processes. However, until now, experimental VLE data involving mixtures of HFO-1234yf, HCFO-1233xf and HCFC-244bb are relatively scarce. Although the VLE data for system of HCFC-244bb + HFO-1234yf have been published in our previous work [11], no systematic experimental data for systems of HFO-1234yf + HCFO-1233xf and HCFO-1233xf + HCFC-244bb have been

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reported in the open literature.

In this paper, the isothermal VLE data for the binary systems of HFO-1234yf + HCFO-1233xf and HCFO-1233xf + HCFC-244bb were measured at 293.15, 303.15, and 313.15 K, and 303.15, 313.15, and 323.15 K, respectively. All of the experimental data were correlated with the Peng–Robinson equations of state in connection with the van der Waals mixing rules. The information presented here is essential to design and optimize the purification process of HFO-1234yf.

2. Experimental

2.1. Chemicals

The samples of HFO-1234yf, HCFO-1233xf and HCFC-244bb were provided by Xi'an Modern Chemistry Research Institute. The purities of the samples were determined by gas chromatography (Shimadzu GC-2010) which is equipped with a flame ionization detector (FID) and a capillary column (PLOT Al$_2$O$_3$ S, Agilent model 19091P-S33). The Gas Chromatography conditions are listed in Table 1. The purities of HFO-1234yf and HCFO-1233xf were found to be better than 0.999 in mass fraction, the purity of HCFC-244bb was above 0.995 in mass fraction. To eliminate the effect of gaseous impurities, the sample was degassed by repeatedly evacuating the sample container immersed in liquid nitrogen. The purities of the samples are summarized in Table 2.

2.2. Apparatus

The experimental apparatus for the VLE measurements in this work has been presented, details can be found in Yang et al. [12]. The experimental apparatus included a VLE cell, a thermostatic bath, a temperature measurement system, a pressure measurement system and a vacuum system. The VLE cell was made of 304-type stainless steel, with two quartz glass windows for observation. The cell was immersed in a thermostatic bath which is also equipped with optical windows. The temperature of thermostatic bath was controlled by a computerized Smith-PID algorithm, and could be varied from approximately 243–453 K. The temperature fluctuation of thermostatic bath was less than ±10 mK. The temperature was measured by a 100-Ω standard platinum resistance thermometer (NANMAC Inc., model T100-650), and the temperature value was determined by a stack thermometer Readout (Fluke, model hart 1560) on the basis of the international temperature scale of 1990 (ITS-90). The total uncertainty in temperature measurements was estimated to be within 20 mK. The pressure was measured by four high-precision absolute pressure sensors (A, B, C, and D, Mensor Inc., models 6100) and a differential pressure transducer (Xian Instrument, model 1151DP). The pressure measurement system could determine the pressure up to 10 MPa. The pressure sensors were used in four different measurement scales with the same accuracy of 0.01%. In this work, the pressure sensor (B) was used to measure the VLE data from (0 to 5 MPa). The total uncertainty of the pressure measurement was estimated to be within 1.5 kPa. The compositions of the coexisting vapor and liquid phases were analyzed by a gas chromatography (Shimadzu, model GC-2010) equipped with a flame ionization detector (FID). The gas

chromatography was connected online to the VLE cell.

2.3. GC calibration

The uncertainty of composition measurement was calibrated by measuring a set of mixtures with known compositions. The mixtures were prepared in vapor phase in stainless steel bottles which were equipped with sampling valves and connected to GC online, as showed in Fig. 1. The method of GC calibration was similar to Bobbo et al. [13], and details can be found in Yang et al. [12]. The bottle's total capacity was about 200 cm^3. The tare weight was about 320 g and the maximum pressure was 3 MPa. The sample bottle could be weighed by a digital balance (Sartorius Inc., BSA423S) with an accuracy of 0.001 g. The estimated uncertainty in mixture preparation was ±0.01 g and ±0.001 in mole fraction. The estimated uncertainty of GC response was ±0.002 in mole fraction considering the calibration factors and GC reproducibility. The total uncertainty of composition measurement for both liquid and vapor phase compositions was estimated to be ±0.005 in mole fraction.

2.4. Measurement procedure

The VLE cell was washed and evacuated at first to remove the residual components. Then, a less volatile component of the mixture was used to purge the VLE cell and evacuated again, and the procedure was repeated for 3 times. After that, an appropriate amount of the pure component was charged into the VLE cell while the thermostatic bath was cooled down. When the temperature fluctuation was less than ±10 mK at desired temperature at least an hour, the vapor pressure of the pure component was recorded. Then the second component of the mixture was charged into the cell. In order to hasten the attainment of equilibrium, the liquid phase within the VLE cell was stirred with a Teflon-coated bar, which was driven by a magnetic stirrer. As the temperature remained constant for more than an hour, the pressure was measured, and the samples of liquid and vapor phase were drawn off for gas chromatograph analysis. The vapor and liquid mole fractions were analyzed at least three times. Repeating the process above by adding the more volatile component step by step, VLE data of other concentration were measured.

3. Data correlations

The VLE data were correlated by the Peng–Robinson (PR) equations of state (EOS) [14] with the van der Waals (vdW) mixing rules [15]. The vdW mixing rule for calculating mixture parameters (a_m and b_m) can be written as:

$$a_m = \sum_{i=1}^{N} \sum_{j=1}^{N} y_i y_j a_{ij} \tag{1}$$

$$b_m = \sum_{i=1}^{N} y_i b_i \tag{2}$$

Table 1
Gas chromatography conditions.

Temperature/K			Column			Flow rate/cm^3 min^{-1}		
Injector	Oven	Detector	Type	Length/m	Diameter/μm	N$_2$	H$_2$	Air
413	413	473	Capillary column	30	320	27	30	400