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Isothermal vapor–liquid equilibrium data for the binary mixture difluoromethane (HFC-32) + ethyl fluoride (HFC-161) over a temperature range from 253.15 K to 303.15 K

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ABSTRACT

Isothermal vapor–liquid equilibrium data of difluoromethane (HFC-32) + ethyl fluoride (HFC-161) mixture in the range of temperatures from 253.15 K to 303.15 K have been measured in the wide range of compositions. The experimental method used for this work is the single-cycle type. Using Peng–Robinson (PR) equation of state, combined with the first Modified Huron-Vidal (MHV1) mixing rule and Wilson model, the vapor–liquid equilibrium data are correlated. The correlation results have a good agreement with the experiment results. The average absolute vapor composition deviation is within 0.0125, and its largest absolute deviation of the vapor composition is 0.0568; the average relative pressure deviation is within 0.76% and its largest relative pressure deviation is 2.87%. In addition, the results reveal that there is no azeotrope in the binary system, and their temperature glides are small.

1. Introduction

HCFCs (hydrochlorofluorocarbons) are important refrigerants in vapor compression refrigeration systems. However, the concern about the depletion of the stratospheric ozone layer by chlorine derived from HCFCs has led to the Montreal Protocol and relative international agreements. The phase-out of HCFCs has stimulated significant research to find suitable replacements in various processes. The most promising alternatives are mixtures of hydrofluorocarbons (HFCs) which offer the possibility of matching several key thermodynamic properties of conventional HCFCs. There is a great deal of interest in binary and ternary refrigerant blends based on the hydrofluorocarbon refrigerant HFC-161 [1–3] due to its excellent thermodynamic performances and environmental characteristics. Though HFC-161 is flammable, the blended refrigerant based on it can be chosen to match the properties of corresponding traditional refrigerants to be replaced. However, the available vapor–liquid equilibrium (VLE) data for these important blended refrigerants are hardly found in the published literatures, except that Chen et al. [4] measured the PVT data in the temperature range from 303 K to 403 K. This will be the obstacle to develop energy-efficient, cost-effective and environment-friendly refrigeration cycles for using the new blended refrigerants. Therefore, VLE data for refrigerant mixture HFC-32 + HFC-161 over the temperature range from 253.15 K to 303.15 K are reported in this paper. In addition, in order to predict the behavior of the binary mixture HFC-32 + HFC-161, accurate thermodynamic models are required, which is essential for the selection of alternative refrigerants and engineering designs.

2. Experiments

The samples of HFC-161 and HFC-32, provided by Zhejiang Lantian Environment Protection Hi-Tech Co., Ltd, have a purity of 99.74 wt% for the HFC-161 with the principal impurities of ethylene and iso-butane, and 99.98 wt% for the HFC-32 with the principal impurity of chloromethane. They were used without further purification.

Data of temperature–pressure–liquid–vapor composition T–p–x–y were obtained from experiments made with a recirculating still. A schematic of the experimental equipment in this work is shown in Fig. 1, which is the same as the one described in detail by Han and Cui [3,5]. It consists of a stainless steel equilibrium cell and temperature and pressure measuring systems, etc. The stainless steel equilibrium cell equipped with double glass windows has a volume of 80 mL. A motor blender, rotated at variable speeds, is used to accelerate the equilibrium process. The temperature of the equilibrium cell in the thermostated bath is maintained by the compression refrigeration cycle and heater. The temperature fluctuation in the bath is less than ±5 mK/30 min. The temperature

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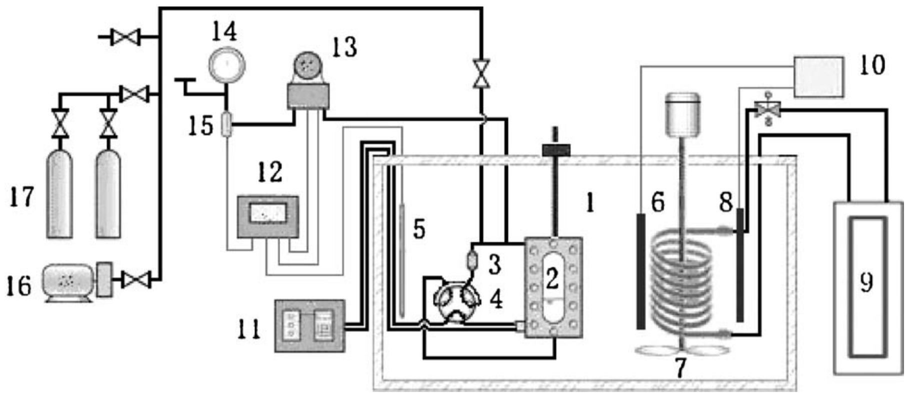

Fig. 1. Experimental apparatus for the VLE measurement: (1) thermostat bath; (2) equilibrium cell; (3) vapor circulation pump; (4) six-way valve; (5) high accuracy platinum resistance thermometer; (6) platinum resistance thermometer; (7) motor blender; (8) heater; (9) refrigeration system; (10) temperature controller; (11) gas chromatograph; (12) digital multimeters; (13) differential pressure null transducer; (14) piston-type pressure gauge; (15) pressure transmitter; (16) vacuum pump; (17) sample reservoir.

is measured by a four-head 25-platinum resistance thermometer (Model: WZPB-2, China) with an uncertainty of ±10 mK (ITS) and a Keithley 2010 data acquisition/switch unit. The overall uncertainty of temperature measured is ±15 mK. The pressure is measured by a pressure transducer (Model: PMP4010, Drunk), a differential pressure null transducer (Model: 1151DP, China), an oil-piston type dead-weight pressure gauge (Model: YS-6·60·250·600, China), and an atmospheric pressure gauge (Model: DYM-1, China). The total uncertainty of the pressure measurement is ±1.6 kPa.

Both vapor and liquid samples are analyzed by gas chromatograph (GC) (Model: GC112A, China) equipped with a flame ionization detector (FID), which is connected to vapor–liquid sampling valves on-line. It is calibrated with pure components of known purity and with mixtures of known composition that were prepared gravimetrically. In order to ensure repeatability, the experimental data at the equilibrium state are measured at least three times. Considering the margin of error and reproducibility of GC, we generally estimate an overall uncertainty in the measurements of the composition of ±0.003 in mole fraction for both the liquid and vapor phases.

The experimental process is as follows. The cell was evacuated to remove the inert gases. A targeted amount of HFC-161 and HFC-32 was introduced into the cell, and the temperature of the entire system was maintained by controlling the temperature of the thermostated bath. The vapor in the cell was circulated continuously by the magnetic circulation pump until an equilibrium state was established. It was believed that 2 h or more was sufficient to obtain thermal equilibrium state between the cell and the thermostated bath. After the equilibrium was achieved at the desired temperature, the pressure in the equilibrium cell was measured. The compositions of samples were measured by immediately injected into GC, which was connected on-line to vapor and liquid sampling devices.

3. Model

In this work, we have used the Peng–Robinson (PR) equation-of-state (EOS) described by Peng and Robinson [6]. Its expression is

$$p = \frac{RT}{v-b} - \frac{a}{v^2+2vb-b^2} \tag{1}$$

$$a = \frac{0.45724\alpha(T)R^2{T_c}^2}{p_c} \tag{2}$$

$$\alpha(T) = \left[1+k\left(1-\left(\frac{T}{T_r}\right)^{0.5}\right)\right]^2 \tag{3}$$

$$k = 0.37464 + 1.54226\omega - 0.26992\omega^2 \tag{4}$$

$$b = \frac{0.07780RT_c}{p_c} \tag{5}$$

where p is the pressure (Pa), v is the molar volume ($\mathrm{m^3\,mol^{-1}}$), T is the absolute temperature (K), R is general gas constant ($\mathrm{J\,mol^{-1}\,K^{-1}}$), T_c is the critical temperature (K), p_c is the critical pressure (Pa), ω is acentric factor, a, b are PR equation of state dependent parameters, respectively.

In our equation of state approach, the mixing rule used to correlate the VLE data is the first modified Huron-Vidal mixing rule (MHV1) of Michelsen [7]

$$\frac{a_m}{b_m RT} = \frac{1}{C^{\mathrm{MHV1}}}\frac{G^E}{RT} + \frac{1}{C^{\mathrm{MHV1}}}\sum_i x_i \ln\left(\frac{b_m}{b_i}\right) + \sum_i x_i \frac{a_i}{b_i RT} \tag{6}$$

$$b_m = \sum_i x_i b_i \tag{7}$$

where G is Gibbs free energy and $C^{\mathrm{MHV1}} = -0.623$ for PR EOS, superscripts E, MHV1 are excess property, the first modified Huron-Vidal mixing rule, respectively, subscript m denotes the mixture, and x_i is liquid mole fraction.

The fugacity coefficient of i component in a mixture is expressed as [8]

$$\ln\hat{\phi}_i = \frac{\partial(nb_m)}{\partial n_i b_m}(Z-1) - \ln(Z-B) - \frac{1}{2\sqrt{2}}\bar{\alpha}\ln\left(\frac{Z+\left(1+\sqrt{2}\right)B}{Z+\left(1-\sqrt{2}\right)B}\right) \tag{8}$$

where

$$B = \frac{b_m p_c}{RT_c} \tag{9}$$

$$\frac{\partial(nb_m)}{\partial n_i} = b_i \tag{10}$$

$$\bar{\alpha} = \frac{1}{n}\frac{\partial\left(n^2\bar{\alpha}\right)}{\partial n_i} = \frac{1}{RT}\left(\sum_i x_i\frac{a_i}{b_i} + RT\frac{1}{C^{\mathrm{MHV1}}}\left(\ln\gamma_i + \ln\frac{b_m}{b_i} + \frac{1}{b_m}\frac{\partial(nb_m)}{\partial n_i} - 1\right)\right) \tag{11}$$

where Z is the compressibility factor of the mixture, γ_i is the activity coefficient of i component, obtained by G^E model.