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A static analytical apparatus for vapour pressures and (vapour + liquid) phase equilibrium measurements with an internal stirrer and view windows

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ABSTRACT

A new static analytical apparatus for reliable vapour pressures and (vapour + liquid) equilibrium data of small-scale cell (≈150 mL) with internal stirrer and view windows was designed. In this work, the compositions of the phases were analyzed by a gas chromatograph connected on-line with TCD detectors. The operating pressure ranges from (0 to 3000) kPa, and the operating temperature range from (293 to 400) K. Phase equilibrium data for previously reported systems were first measured to test the credibility of the newly developed apparatus. The test included vapour pressure of 1,1,1,3,3-pentafluoropropane (R245fa) and isobutane (R600a), VLE of the (R600a + R245fa) system from $T = (293.150 \text{ to } 343.880)$ K. The measured VLE data are regressed with thermodynamic models using Peng–Robinson EoS with two different models, *viz.* the van der Waals mixing rule, and the Huron–Vidal mixing rule utilising the non-random two-liquid activity coefficient model. Thermodynamic consistency testing is also performed for the newly measured experimental data.

1. Introduction

Organic-fluid mixtures have received increasing attention as working media for refrigeration, heat pump and power generation cycles due to their potential for environment-friendly and their favourable characteristics for improving system performance [1–3]. Phase equilibrium data are of great importance in calculation of thermodynamics properties and optimization of thermodynamics cycles.

The objective of this paper is to provide a new static analytical apparatus with internal stirrer and view windows for reliable vapour pressures and (vapour + liquid) equilibrium data of pure and mixed organic fluids above room temperature. The (R600a + R245fa) system was selected to test the credibility of the apparatus. The data of the saturated vapour pressures were correlated by a Wagner type equation [4], and the VLE data were correlated with thermodynamic models using Peng–Robinson EoS (PR EoS) [5] with two different models, namely the van der Waals (vDW) mixing rule [6], and the Huron–Vidal (HV) mixing rule [7] utilising the non-random two-liquid (NRTL) activity coefficient model [8]. To the best of our knowledge, the experimental data of (R600a + R245fa) system is reported by Sbobb *et al.* [9]. The detailed comparisons will be presented in the following sections.

2. Experiment description and theoretical models

2.1. Equilibrium apparatus

The apparatus designed in this paper is based on the static-analytic method with an internal stirrer and view windows which allows for the analysis of vapour pressure and (vapour + liquid) phase at equilibrium. A schematic of the apparatus is shown in figure 1.

2.1.1. Equilibrium cell

The equilibrium cell consists of the cell assembly and an internal stirrer. The cell was made of stainless steel with the volume of 150 mL and enclosed with two Si–Al glasses each held by two mobile flanges. There are two other flanges and a charging port on the cell wall. The upper flange is used to hold the internal stirrer. The lower flange containing four different diameters holes restricts different diameters capillaries to enter into the equilibrium cell for sampling (one vapour-phase capillary at the top of

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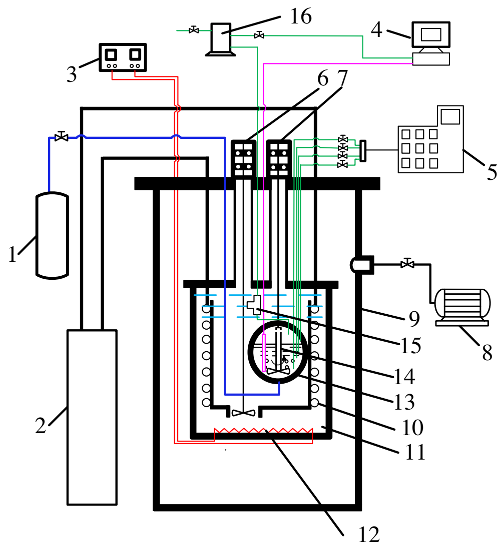

FIGURE 1. A schematic of the experimental apparatus. 1. Feed system; 2. Digital controller; 3. Digital controller; 4. Temperature and pressure indicator; 5. GC; 6,7. Motors; 8. Vacuum pump; 9. Vacuum vessel; 10. Cooling coil; 11. isothermal liquid bath; 12. Electric heater; 13. Equilibrium cell; 14. Stirrers; 15. Pressure transducer; 16. N_2-filled system.

the cell and three liquid-phase capillaries at different elevation with 0.35 mm inner diameter in the cell) and pressure measurement lines with 0.5 mm inner diameters. The internal stirrer contains an axis with many blades and two ceramic bearings, which is controlled by a speed controller.

2.1.2. Isothermal environment for the equilibrium cell

In this apparatus, the equilibrium cell is immersed into the isothermal liquid bath. Silicone oil is used as the heating medium in the liquid bath for high temperatures. In order to decrease heat leaks, the equilibrium cell is fixed a suitable position within the oil bath that about 50 mm of the oil is above the upper of the equilibrium cell. To overcome the heat losses at high temperatures, a vacuum environment and thermal insulation materials surround thermostatic bath. A 100 Ω standard platinum resistance thermometer is inserted into the bath to monitor temperatures of the bath. A 25 Ω standard platinum resistance thermometer is used to measure the temperatures of the equilibrium cell and inserted into the cell with a 316 stainless steel casing. The oil bath temperature is controlled by adjusting the heat loads of cooling water and an electric heater using Shimaden SR 253 digital controllers. A stirrer with a speed controller is located in the liquid bath to obtain uniform temperature distributions.

2.1.3. Sampling method

The accurate sampling for vapour and liquid phase is achieved using a six-port-automatic-sample-injection (SPASI) valve equipped with the GC in which the sample is loaded through four stainless steel capillaries with the same 0.35 mm internal diameters and fine needle valves in the front of SPASI valve. The capillaries lied in different height for vapour and liquid sampling are welded in the flanges of thermostat bath and vacuum vessel, and the parts exposed in environment are held a temperature close to oil bath temperature maintained by electric heat bands. The needle valves from Swagelok are turned off when no sampling is taken. Figure 2 shows a schematic flow diagram of the SPASI value. In the pushing mode, the sample quantitative loop is loaded through the capillaries. In the sample mode, rotation of the rotor 60°, the sample in the loop is injected in the chromatographic column and analyzed. This sampling method provides a tiny dead volume neglected comparing the volume of the cell to avoid the influence to the equilibrium state in the cell. Since the sample system is isolated, there was no change in interior conditions for the sample.

2.1.4. Pressure, temperature and composition measurements

The pressure measurement system includes a digital pressure transducer (Mensor CPT6001) and a sensitive diaphragm pressure transducer (GE DRUCK). The accuracy of digital pressure transducer is 0.01% FS over the ranges of (0 to 1.5) MPa and (0 to 3) MPa. The diaphragm pressure transducer separates the sample from an N_2-filled system with the digital pressure transducer. The accuracy of the transducer is 0.04% FS with the pressure difference adjustable range of (0 to 40) kPa and the temperature range is (233 to 400) K. The combined uncertainty of pressure measurement is estimated to be within ±500 Pa.

A 25 Ω standard platinum resistance thermometer (calibrated by the Cryogenic Metrology Station of the Chinese Academy of Sciences based on the 1990 International Temperature Scale (ITS 90)) is used for temperature measurements (with a uncertainty of ±5 mK ($k = 2$)). The temperature values are logged using the FLUKE 1594A data acquisition unit. The total uncertainty of the temperature measurement is estimated to within ±5 mK.

The compositions of the phase in equilibrium cell are analyzed by a Shimadzu GC2014 gas chromatograph equipped with a thermal conductivity detector (TCD). The GC must be calibrated with mixtures of known composition obtained gravimetrically before the VLE data are measured. The uncertainties of vapour and liquid mole fractions measurements are estimated to be less than ±0.005.

2.2. Experimental procedure

The experimental system is evacuated using an oil vacuum pump. Then a certain amount of the less volatile component is introduced into the cell. In the experimental process, the temperature controller is set to the desired temperature and the internal stirrer is started. When the temperature in the cell reaches the desired value for at least 1 h and the fluctuation in the cell is less than ±3 mK for at least 10 min, the equilibrium state is considered to be achieved. Then the saturated vapour pressures of the first component can be obtained. Then the appropriate more volatile component is then forced into the cell. Once equilibrium is established, samples of the the vapour and liquid phases are taken. The six-way automatic sampling valve could be used to clean the capillary and sample quantitatively. The vapour and liquid mole fractions at the equilibrium state are measured by the on-line gas chromatograph. At least 3 samples leading to a repeatable mole fraction within 0.2% are taken. VLE data for other compositions are measured by introducing an adequate amount of the more volatile component step by step. At last, the cell is evacuated and the saturated vapour pressures of the more volatile pure component are measured.

2.3. Theoretical models

2.3.1. Statured vapour pressures

The experimental data of statured vapour pressures were correlated by a Wagner type equation [4]. The Wagner type equation is given by the expression:

$$\ln \frac{p}{p_c} = \frac{T_c}{T}(a_0\tau + a_1\tau^{1.5} + a_2\tau^{2.5} + a_3\tau^5), \tag{1}$$

$$\tau = 1 - \frac{T}{T_c}, \tag{2}$$