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Isothermal vapor–liquid equilibria for binary mixtures of benzene, toluene, m-xylene, and N-methylformamide at 333.15 K and 353.15 K

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ABSTRACT

Isothermal vapor–liquid equilibrium (VLE) at 333.15 K and 353.15 K for four binary mixtures of benzene + toluene, benzene + N-methylformamide, toluene + m-xylene and toluene + N-methylformamide have been obtained at pressures ranged from 0 kPa to 101.3 kPa. The NRTL, UNIQUAC and Wilson activity coefficient models have been employed to correlate experimental pressures and liquid mole fractions. The non-ideal behavior of the vapor phase has been considered by using the Soave–Redlich–Kwong equation of state in calculating the vapor mole fraction. Liquid and vapor densities were also measured by using two vibrating tube densitometers. The *P*–*x*–*y* diagram and the activity coefficient indicate that two mixtures of benzene + toluene and toluene + m-xylene were close to the ideal solution. However, two mixtures containing N-methylformamide present a large positive deviation from the ideal solution. The excess Gibbs energy in the benzene + toluene mixture is negative indicates that it is an exothermic system.

1. Introduction

Vapor–liquid equilibrium (VLE) data are essential for engineering design of separation processes and unit operations. It is useful for the extension of thermodynamic models commonly applied for petrochemical related industries. Such information can be obtained experimentally or adopted from generalized methods to calculate properties of multi-component mixtures. Accurate densities of vapor and liquid phases are critical and important to result in a proper size in the process design of many separation equipments. For an ideal system, it is relatively easy to estimate vapor–liquid equilibrium. However, most liquid systems of industrial interest show deviations from the ideal behavior. Raal and Muhlbauer describe with detail a few commonly used liquid phase activity coefficient models [1]. Klara et al. [2], Huang et al. [3], Gultekin [4] successfully correlate their *P*–*T*–*x*–*y* data of benzene + toluene and toluene + N-formylmorpholine (NFM) mixtures with the NRTL, UNIQUAC and Wilson models. In their studies, binary interaction parameters of mixtures were obtained to predict phase behavior by examining experimental data for thermodynamic consistency. Santiago et al. [5] correlates the VLE data by a few activity coefficient models for a ternary system of ethanol + 2-methyl-1-butanol + calcium chloride. Simoni et al. [6] models the L–L equilibria of ionic liquid systems with NRTL, electrolyte-NRTL and UNIQUAC models. These liquid-activity models with optimally fitted binary parameters have then been employed to predict phase behaviors of the VLE and LLE systems. Densities of the benzene + toluene mixture have been analyzed using refractive index measurements by Sumer and Thompson [7]. To our knowledge, isothermal VLE data for a system of N-methylformamide + toluene have not been found in the literature.

In this study, experimental *P*–*x* data were measured at 333.15 K and 353.15 K under pressure ranged from 0 kPa to 101.3 kPa for four binary mixtures of benzene + toluene, benzene + N-methylformamide, toluene + m-xylene and toluene + N-methylformamide by using the isothermal bubble-point pressure method. These experimental data (P, x_i) were then used to obtain vapor mole fraction (y_i), activity coefficient (γ_i) and the system excess molar Gibbs free energies (G^E). Finally, the phase equilibrium calculation was carried out by adopting the Soave–Redlich–Kwong (SRK) equation of state [8] for the vapor phase and the Wilson [9], NRTL [10] and UNIQUAC [11] activity coefficient models for the liquid phase.

2. Experimental

2.1. Chemicals

De-ionized water was prepared using a Milli-Q purification system and 99.99% nitrogen was obtained from Air Product Co.

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(Taiwan). Both are used for calibration of pressure and temperature related constants for two densitometers. All the chemicals were high-purity grade purchased from a local supplier, such as, benzene (Fluka, ≥99.5% pure), toluene (Sigma, ≥99% pure), m-xylene (Alfa Aesar, ≥99% pure) and N-methylformamide (Sigma, ≥99% pure) used as reagents without further purification.

2.2. Apparatus and procedures

The equilibrium system was previously designed by Chang et al. [12] and used with a little modification. Temperature studied at 333.15 K and 353.15 K and pressure measured from 0 kPa to 101.3 kPa. Fig. 1 shows the system mainly consists of a 80 mL equilibrium cell (9) equipped with a side-view glass window, a digital pressure transducer (13), a data acquisition set (17a) and two densitometers (17b, 17c). Two magnetic circulation pumps (11a, 11b) were used to speed up the achievement of the equilibrium, which is a mixed device of static and dynamic methods.

In each experiment, the cell was first charged with 50 mL of a pure liquid or a binary mixture with a certain composition. Then, system pressure reached the bubble-point of the liquid by using a vacuum pump (15) operation. At this pressure, temperature of the cell was indicated by a K-type digital thermometer (12) and controlled within ±0.01 K by an air bath (8). Equilibrium was usually reached after 20 min, then, the unchanged vibration periods of the liquid and vapor phases were recorded by a printer (16). Vibration periods of vapor and liquid phases were measured by two densitometers (Anton-Paar, DMA512 and DMA512P) and a digital data processor (DMA60). The temperature in the vibrating-tube housing of the densitometer was thermally controlled by a high-precision circulator (Julabo, F10-HC) (4) at the same temperature of the cell. The temperature in the circulator was determined using a standard platinum thermometer (Hart Scientific, model 1506) (14). An equilibrium state was assured when the vibration period of the density tube is stable at least for 2 min. Densities of two phases can be obtained from individual calibration equation described by Chang and Chen [13]. The apparatus employed for the density calibration by using a N_2 cylinder (1), a metering pump (3), a few valves (6, 7a, 7b, 7c), a Boudon pressure gauge (5) and a solvent collector (18), also shown in Fig. 1.

At a V–L equilibrium, the experimental liquid phase composition (x) was obtained by using a corresponding equation of $x = a\rho + b$ from the measured density (ρ) at known liquid phase composition. The regression coefficients of these straight lines all attain 0.999. The correction of liquid phase composition shows that the deviation between the experimental and the prepared liquid composition is less than 0.001. The largest deviation of the toluene + m-xylene system is also within 0.003. The densitometer has a repeatability of about $5(10)^{-5}$ g/cm^3, the electronic balance has the minimum reading about $1(10)^{-5}$ g, the variation of the temperature was found to be less than ±0.01 K, the accuracy of the pressure reading was within ±0.1% for the full scale, and the liquid mole fraction of each component (x_i) was estimated to be deviated within ±0.003.

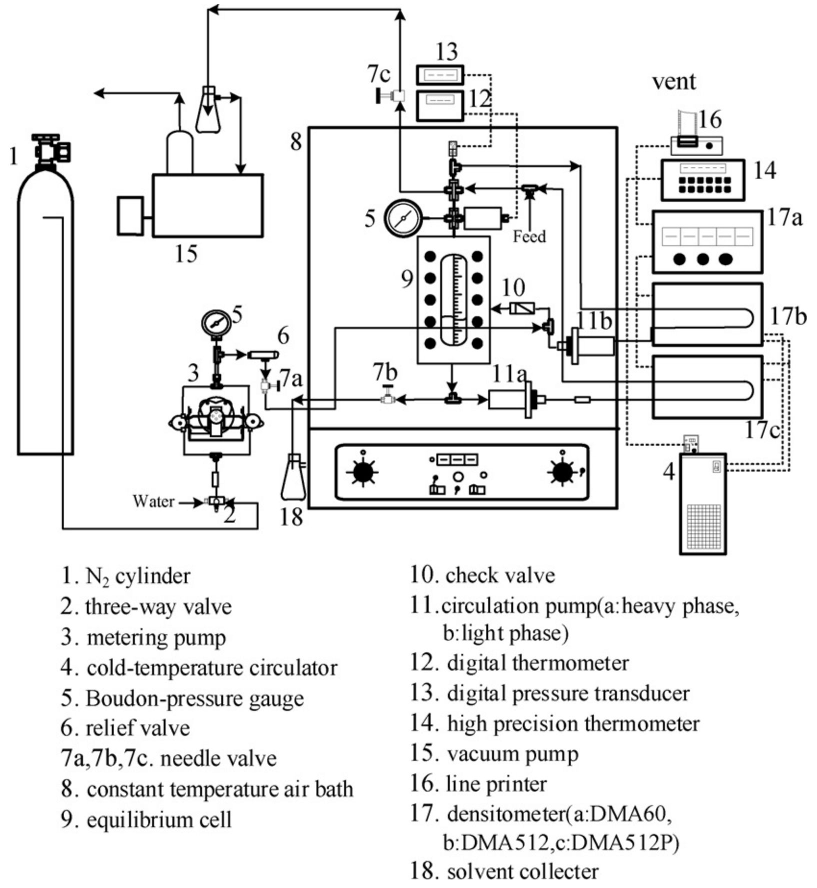

Fig. 1. Schematic flow diagram of an experimental setup for vapor–liquid phase equilibrium measurement. (1) N_2 cylinder, (2) three-way valve, (3) metering pump, (4) cold-temperature circulator, (5) Boudon-pressure gauge, (6) relief valve, (7a, 7b, 7c) needle valve, (8) constant temperature air bath, (9) equilibrium cell, (10) check valve, (11) circulation pump (a: heavy phase, b: light phase), (12) digital thermometer, (13) digital pressure transducer, (14) high precision thermometer, (15) vacuum pump, (16) line printer, (17) densitometer (a: DMA60, b: DMA512, c: DMA512P), and (18) solvent collector.