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Experimental determination of critical data of multi-component mixtures containing potential gasoline additives 2-butanol by a flow-type apparatus



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ABSTRACT

In this work, we used a flow method for measurement of critical properties of six binary mixtures (2-butanol + cyclohexane, 2-butanol + hexane, 2-butanol + heptane, 2-butanol + octane, 2-butanol + nonane and 2-butanol + decane) and two ternary mixtures (2-butanol + hexane + heptane and 2-butanol + octane + decane). The critical properties were determined by observing the disappearance and reappearance of the gas-liquid phase meniscus in a quartz glass tube. The standard uncertainties of temperatures and pressures for both binary and ternary mixtures were estimated to be less than 0.2 K and 5.2 kPa, respectively. These critical data provide the boundaries of the two-phase regions of the related mixture systems. Six binary systems show non-ideal behaviors in the loci of critical temperatures. We used the Redlich-Kister equations to correlate the critical temperatures and pressures of these systems and listed the binary interaction parameters. The maximum average absolute deviation (AAD) of each binary system between experimental data and calculated results from Redlich-Kister equations is 0.038% for critical temperatures, and 0.244% for critical pressures. Moreover, the two ternary systems were newly reported and correlated by Cibulka's and Singh's expressions. The maximum AAD of critical temperatures and critical pressures are 0.103% and 0.433%, respectively.

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1. Introduction

With the developing of transportation and the increasing requirement of electricity, the scarcity of fuel resources becomes more and more serious. Many chemical engineers pay their attention on the developments of petroleum collection, crude oil recovery, and internal combustion engine [1]. Cyclohexane, hexane, heptane, octane, nonane and decane are all fundamental components of fuels and intermediate products in petrochemical industry [2]. Their mixtures are often applied as ignition surrogates of diesel and gasoline in researching reports [3-5]. 2-butanol is a higher alcohol which has good potential for using as additive in gasoline because of their favorable properties, such as lower vapor pressure, higher energy density, lower affinity for water and potentially improved material compatibility. It can be produced by extraction from synthesis gas, fermentation from sugars and conversion from mixtures of alcohols [6]. Understanding the behavior of mixtures of these hydrocarbon fuels and higher alcohol is especially crucial for the development of flex fuel vehicles [7,8]. Critical properties of

* Corresponding author. E-mail address: mghe@mail.xjtu.edu.cn (M. He). these mixtures are also significant important in theoretical prediction of other thermodynamic properties, because they reflect the real behavior and provide the location and border of the twophase region. The accuracy of predicting methods using equations of states, corresponding states principle and renormalization group theory are largely depends on the accuracy of critical properties [9,10]. However, the critical data of these mixtures are rather scarce and most of them are predicting results.

Currently, some scholars have focused their work on critical properties of mixtures of hydrocarbon fuels and gasoline additives. Soo [11] measured the critical data of azeotropic systems ethanol + n-alkanes (C_4-C_8) and plotted the critical surfaces of pentane + ethanol + hexane system. Wang [4] determined the critical temperatures and pressures of three binary and two ternary mixtures including methanol, 1-propanol, heptane and methyl tert-butyl ether. Gil [12] measured a series of critical properties of n-hexane + alkan-1-ol. Morton [13] also reported the critical data for (alkanol + alkane) mixtures, which include secondary or tertiary alcohols and/or branch chain alkanes. In this work, we applied a flow method apparatus to measure the critical temperatures and critical pressures of a series of mixtures containing 2-butanol (2-butanol + cyclohexane, 2-butanol + hexane, 2-butanol + heptane,







2-butanol + octane, 2-butanol + nonane, 2-butanol + decane, 2butanol + hexane + heptane and 2-butanol + octane + decane). The experimental results of all binary mixtures were newly reported. We correlated the critical properties of binary systems with the Redlich–Kister equations and listed the binary interaction parameters of each system. We also correlated the critical properties of ternary systems with the Cibulka's expressions and Singh's expressions, and compared the calculate results of them.

2. Materials and methods

2.1. Materials

Table 1 summarizes the details of purities and suppliers of the compounds used in this study. The purities of compounds were all above 0.990 which checked by gas chromatograph. They were directly used without further purification in this work.

2.2. Apparatus and procedure

A typical flow-type apparatus was applied to determine the critical temperatures and pressures in this study. The principle of flow method was first presented by Rosenthal and Teja [14] and widely used in measuring critical properties [15–18]. The critical point was determined by observing critical opalescence and phase changes in the cell. The apparatus was designed in our previous work [19]. The quartz glass cell can be operated at temperatures up to 773 K and pressures up to 10 MPa. A more detailed description of apparatus and experimental procedure has been reported in our previous work [19]. So we just give a brief description here.

The apparatus is presented in Fig. 1. Before the experiment, the flow path of the apparatus was evacuated with inert gas. The hydrocarbon and 2-butanol reagents were weighted by an electronic balance (Mettler Toledo ME204, 0.001 g) and mixed uniformity in a sample bottle. Then, the mixed reagent was pumped rapidly through the flow path by a dual piston pump (LabAlliance

Table 1

Purity and source of the used compounds^a.

Compounds	Purity (mass)	Source	Analysis method
2-Butanol	>0.995	Aladdin, Shanghai, China	Gas chromatography
Hexane	>0.995	Guangfu, Tianjin, China	Gas chromatography
Cyclohexane	>0.995	Guangfu, Tianjin, China	Gas chromatography
Heptane	>0.995	Guangfu, Tianjin, China	Gas chromatography
Octane	>0.990	Guangfu, Tianjin, China	Gas chromatography
Nonane	>0.990	Guangfu, Tianjin, China	Gas chromatography
Decane	>0.990	Guangfu, Tianjin, China	Gas chromatography

^a All compounds were used without any further purification.



Fig. 1. Experimental system of the low-resident time flow method. ST, sample tank; DP, dual piston pump; V, valve; VP, vacuum pump; PH, preheater; TC, thermocouple; PRT, platinum resistance thermometer; PT, pressure transducer; BV, back pressure valve.

1500, flow control: 0.001 mL/min). This pump can control the fluid with uniform flow rate. In mixture system, the component with lower critical temperature may vaporize and disappear faster from the cell than that with higher critical temperature in the heating process. So the flow rate was commonly controlled more than 6 mL/min to reduce the resident time of the fluid at high temperatures and compensate for this effect. The mixed reagent flowed through the flow path into a view cell which is a thick quartz glass tube. An electric heating furnace was designed outside of the view cell for heating the reagent. The heating power of furnace was controlled by a PID temperature regulator (Shimaden FP23, PID: 0.1). A platinum resistance thermometer probe (Fluke 5608-12 PRT, measurement uncertainty: ±0.02 K) was directly inserted into the glass tube to measure the temperature. A pressure transducer (Rosemount 3051S; 0-10 Mpa, accuracy: ±0.025%) was placed behind the upper outlet of the cell to determine the pressure. All sensor signals from thermometer and pressure transducer were collected by a digital multimeter (Keithley, 2002) and sent to computer. When the mixed reagent flowed through the whole flow path and began to drip into the waste liquid bottle, we confirmed that the flow path was filled with liquid. Then heated the view cell, we could find the liquid flashing. Turned down back pressure valve and increased the pressure, this phenomenon quickly disappeared. The meniscus between vapor and liquid phases of the reagent could be seen clearly from observation window. With the temperature gradually approaching to the critical point, the gas-liquid meniscus became faint and a distinct red-black critical opalescence appeared. This phenomenon was caused by the fluctuation of density near the critical point [20], refractive index fluctuated with the density, and the light irradiated from the back observation window to the view cell was scattering. After temperature exceeded the critical point, the opalescence became more and more faint and vanished with meniscus at last. Only one transparent phase was left. Then, cooled down the view cell, the temperature of reagent gradually approached to the critical value. The transparent phase changed to yellow, to red and finally to black, the critical opalescence reappeared simultaneously. Continue decreasing the temperature, the laver of opalescence gradually became thick but colorless. Finally, opalescence disappeared, gas phase and liquid phase formed, the meniscus reappeared. The reagent was assumed reached critical temperature at the point which meniscus disappeared and reappeared. The critical pressure of the reagent was obtained by observing the meniscus and opalescence too. If the pressure of reagent exceeded critical point, the gas-liquid meniscus would never appear during the heating process. If the pressure below to critical point, the reagent would boil at critical temperature and opalescence would not appear. The pressure at which we could see most distinct opalescence was assumed as the critical pressure. Pressure can be adjusted exactly in our apparatus while the temperature remains constant, which can effectively reduce uncertainty of measurement repeatability of pressure. The critical point of each component was carefully observed for more than three times at different flow rates. We also repeatedly changed the temperature and pressure until the gasliquid meniscus disappeared and reappeared nearly at the same point. Each critical data were measured three times in this work, the average value of them was recorded as the final critical point. Similar apparatus and experimental produce have also been used in works of Soo [11], Gil [12] and Horstmann [21,22]. The veracity and repeatability of our apparatus has been checked by measuring the critical points of nine pure compounds, twenty-two binary systems and seven ternary systems [19,23-25].

The standard uncertainties of temperature, pressure and mole fraction in this work were estimated to be less than 0.2 K, 5.2 kPa and 0.006. The assessment of uncertainties is summarized in supplementary material (Table S1).

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