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Determination of critical properties for binary and ternary mixtures containing propanol and alkanes using a flow view-type apparatus

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ABSTRACT

The critical temperatures and pressures of eight binary systems and two ternary systems (1-propanol + cyclohexane, 1-propanol + *n*-hexane, 1-propanol + *n*-heptane, 1-propanol + *n*-octane, 1-propanol + *n*-decane, 2-propanol + cyclohexane, cyclohexane + *n*-hexane, cyclohexane + *n*-heptane, 1-propanol + cyclohexane + *n*-heptane and 1-propanol + *n*-octane + *n*-decane) were measured using an efficient and accurate low residence time flow apparatus. The uncertainties of the critical temperature and the pressure were estimated to be less than 0.4 K and 0.01 MPa, respectively. All the critical loci of binary systems belong to the type I or type II as defined by Scott and van Konynenburg. The curves of critical temperatures for the six binary mixtures containing 1-propanol or 2-propanol are non-ideal. Maximum average absolute deviations of the Redlich–Kister equations from the experimental results for the critical temperatures and the critical pressures of all the binary systems are 0.05% and 0.07%, respectively. Moreover, the two ternary systems were correlated by Cibulka's and Singh's expressions with maximum average absolute deviations 0.06% for critical temperatures and 0.83% for critical pressures.

1. Introduction

Fluids in supercritical area have many favorable characteristics, such as high diffusion coefficient, low viscosity and good solubility. Supercritical fluids are widely applied in chemical reaction, material processing and industrial extraction [1–5]. In these processes, supercritical fluids usually contain two or more components. Therefore, the critical properties of both pure compounds and mixtures are essential for supercritical fluid technology. As a description of the phase change boundaries in mixture phase diagrams, the critical properties are also necessary in calculating transport properties, *pvT* properties using EOS and the corresponding states principle [6,7]. However, it is difficult to predict the critical properties for other types of fluid phase situations, especially for mixtures. Sengers et al. [8] used the rectilinear scaling law to predict the critical properties. Kiselev [9] predicted the critical properties with the rigorous renormalization group theory. Nonetheless, fluids express the high compressibility near the critical region. Slight perturbations of pressure generate strong density fluctuations. It makes the *pvT* properties of mixture difficult to measure and extrapolate near the critical region. Semiempirical equations method [10] is the most efficient and accurate way to predict the critical properties but it depends on the accurate experimental data.

Cyclohexane, *n*-hexane, *n*-heptane, *n*-octane and *n*-decane are the fundamental materials in chemical engineering, and are the main components of fuel [11]. 1-propanol and 2-propanol are common gasoline additives due to their low exhaust emission, good solubility and environmental friendliness [12,13], and they are also used as bactericide and deicing agent in gasoline, respectively. The critical properties of their mixtures are widely used in composition simulation of petroleum fluid and predicting the behavior in auto-engine [14–16]. In this work, we used a flow apparatus to determine the critical temperatures and critical pressures of a series of mixtures containing 1-propanol (1-propanol + cyclohexane, 1-propanol + *n*-hexane, 1-propanol + *n*-heptane, 1-propanol + *n*-octane, 1-propanol + *n*-decane, 1-propanol + cyclohexane + *n*-heptane and 1-propanol + *n*-octane + *n*-decane) and containing cyclohexane (2-propanol + cyclohexane, cyclohexane + *n*-hexane, cyclohexane + *n*-heptane). The critical data of cyclohexane + *n*-hexane [17,18], cyclohexane + *n*-heptane [17], 1-propanol + *n*-hexane [19,20], 1-propanol + *n*-heptane [20,21] and 1-propanol + *n*-octane [20] agree well with the literatures. The experimental data of all binary mixtures were correlated with the Redlich–Kister equations. The two ternary mixtures are newly reported and correlated with Cibulka's and Singh's expressions.

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Table 1
Purity and supplier of the used chemicals, critical properties of pure substances obtained in this work and those recommended by the National Institute of Standards and Technology, NIST.

Compounds	Purity	Supplier	This work[a]		NIST [22]	
			T_c (K)	p_c (MPa)	T_c (K)	p_c (MPa)
1-Propanol	>0.995	Aladdin, Shanghai, China	536.63	5.167	536.9 ± 0.8	5.20 ± 0.10
2-Propanol	>0.995	Aladdin, Shanghai, China	508.26	4.763	509.0 ± 2.0	4.90 ± 0.50
n-Hexane	>0.995	Guangfu, Tianjin, China	507.79	3.033	507.6 ± 0.5	3.02 ± 0.04
Cyclohexane	>0.995	Guangfu, Tianjin, China	553.61	4.074	554.0 ± 1.0	4.07 ± 0.05
n-Heptane	>0.995	Guangfu, Tianjin, China	540.14	2.736	540.0 ± 2.0	2.74 ± 0.03
n-Octane	>0.990	Guangfu, Tianjin, China	568.92	2.496	568.9 ± 0.5	2.49 ± 0.01
n-Decane	>0.990	Guangfu, Tianjin, China	617.73	2.106	617.8 ± 0.7	2.11 ± 0.08

[a] Standard uncertainties $u(T_c) = \pm 0.4$ K, and $u(p_c) = \pm 0.01$ MPa.

2. Materials and methods

2.1. Materials

The compounds used in this work were used without any further purification since their mass purities are above 0.990. Table 1 shows the details of their purities, suppliers and critical properties obtained in this work, as well as the critical data recommended by the National Institute of Standards and Technology (NIST) [22].

2.2. Apparatus

In this work, we used a flow view-type apparatus, which based on the work of Roess [23] and Rosenthal and Teja [24], to determine the critical properties. A detailed description of the apparatus and experimental procedure was presented in our previous work [25,26]. The reliability and repeatability of the apparatus were checked by measuring the critical properties of eight pure compounds, fourteen binary systems and two ternary systems. We just give a brief description here. The experimental setup used in this work is shown in Fig. 1. Reagents weighed by an electronic balance (Mettler Toledo ME204, 0.001 g) and mixed in a sample tank. The mixed reagent pumped by a dual piston pump (LabAlliance 1500, flow control: 0.001 mL/min) and flows through a view cell with heating and pressuring. An electric heating furnace was designed outside of the view cell and controlled by a temperature controller (Shimaden FP23, PID: 0.1). The heating furnace was filled with silica fiber particles to make the heaters heating the view cell uniformity. A temperature sensor (Fluke 5608-12 PRT, measurement uncertainty: ±0.02 K) was inserted into the glass tube directly to measure the temperature. The pressure of the system is measured by a pressure transducer (Rosemount 3051S; 0–10 MPa, accuracy: ±0.025%). All sensor signals of temperatures and pressures were collected by a digital multimeter (Keithley 2002). The critical points are determined by observing the disappearance and reappearance of the meniscus [27]. In this process, the critical temperature and pressure can be obtained at the same time. And the pressure can be regulated exactly while the temperature remains constant, which reduces the uncertainty of pressure effectively. Similar apparatus have also been used in previous works of Soo et al. [28], Gil et al. [19] and Horstmann et al. [29]. The quartz glass tube cell in this work can be operated up to 10 MPa and the maximum temperature is 773 K.

2.3. Experimental procedure

The critical properties of compounds and their mixtures were determined by observing critical opalescence and the phase changes in the cell as described previously [25]. Before the measurement, the substances were disposed by ultrasonic degas and mixed as the experiment plan, the flow path was evacuated by a vacuum pump. Then, the reagent was pumped rapidly through the flow path with uniform flow rate, and the reagent was seen in the view cell. Thermal decomposition or reaction was minimized because the residence time of the fluid at high temperatures was kept low. Heated the view cell, it was seen considerable flashing of the liquid. Increased the pressure of system, this phenomenon was no longer visible. As the temperature of the reagent gradually approaching to the critical point, the gas–liquid meniscus became faint and eventually vanished. During this processes, the critical opalescence could be observed. After the critical point was exceeded, the critical opalescence vanished and the meniscus disappeared, only one transparent phase was left. Then decreased the temperature to the critical value slowly, the reagent color went from colorless to yellow, to red, and to black, the critical opalescence reappeared. Then the opalescent layer became thick but

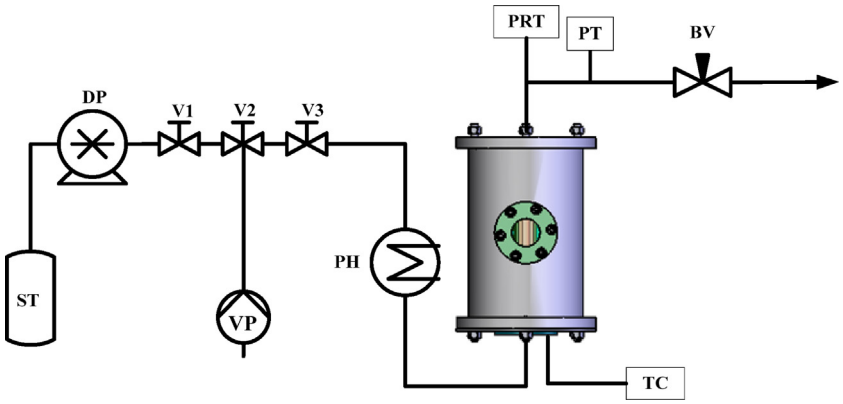

Fig. 1. Experimental system of the low-residence time flow method. ST, sample tank; DP, dual piston pump; V, valve; VP, vacuum pump; PH, preheater; TC, thermocouple; PRT, platinum resistance thermometer; PT, pressure transducer; BV, back pressure valve.