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Determination of critical properties for binary and ternary mixtures of short chain alcohols and alkanes using a flow apparatus

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ABSTRACT

The critical temperatures and pressures of four binary systems and two ternary systems containing gasoline additives (ethanol + cyclohexane, ethanol + octane, 2-propanol + octane, 2-propanol + decane, ethanol + cyclohexane + octane and 2-propanol + octane + decane) were measured with a low-residence time flow apparatus. The critical properties were determined by observing critical opalescence and phase changes in a quartz glass tube. The expanded uncertainties of critical temperature and pressure were estimated to be less than ±0.4 K and ±0.01 MPa, respectively. The four binary systems show non-ideal behavior especially for ethanol + cyclohexane and ethanol + octane systems. The experimental data of all binary mixtures could be correlated to within 0.06% with the Redlich–Kister equations. Ternary mixtures are newly reported in this work and were correlated with Cibulka's and Singh's expressions.

1. Introduction

Critical properties are important basic thermophysical properties for chemical compounds and their mixtures. They are essential for supercritical fluid technology that is widely used in industrial extraction and chemical reaction processes [1–4]. Critical properties are commonly used in the theorem of corresponding states to predict many thermodynamic properties when only limited amount of experimental data are available [5,6]. The reliability of estimated property values largely depends on the reliability of critical properties. Experimental critical data of mixtures, especially those containing more than two compounds, are rather scarce, which limits the development of the predictive methods. Therefore, it is necessary to measure experimental critical properties for both research and engineering applications.

Common experimental methods for measuring critical properties include the sealed-tube method, open-tube method, flow method, laser interferometry method, and *pvT* method [7]. As the density of substance usually has irregular fluctuations near the critical region, the system's stability is poor, so that slight perturbations in the conditions will produce large fluctuations in the measured properties. For most organic substances, the visual method is generally the best technique to measure the critical temperature [8]. This method determines the critical state by observing the disappearance and reappearance of the meniscus with changes in temperature. The temperature difference between disappearance and reappearance of the meniscus can be less than 0.1 K for some compounds [9]. As one type of visual method, the flow method [10–15] is widely used in measuring critical properties of both pure compounds and their mixtures, since the critical temperature and critical pressure can be measured at the same time. The pressure of the measured fluid can be regulated exactly (less than 5 kPa) when the temperature remains constant so that the flow method can measure critical pressure with lower uncertainty than other methods.

The critical properties of petroleum fluids affect compositional simulation of gasoline; the behavior of a petroleum fluid during a chemical reaction can be predicted with its phase diagram and the critical point. Critical properties are also important in design of EoR (Enhanced oil Recovery) projects; the minimum miscibility pressure (MMP), which is a key parameter in the design of a gas injection project, is the critical pressure of complex mixtures [16]. Cyclohexane, octane and decane are all common components of fuel [17]. Short chain alcohols are widely used as gasoline additives for their simple preparation process and excellent properties, such as low exhaust emission, high octane number and environmental friendliness. The addition of ethanol to gasoline not only increases Reid vapor pressure (RVP), but also dramatically decreases the carbon monoxide (CO) and hydrocarbon compounds (HC) emissions [18]. In this research 2-propanol was chosen to study since it can reduce the CO emissions and it can change the ignition delay of blended fuels [19,20]. The critical temperatures and

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Table 1
Supplier and purities of the used chemicals and critical properties for pure substances used in the Redlich–Kister equations.

Compounds	Purity	Supplier	This work[a]		NIST [25]	
			T_c/K	p_c/MPa	T_c/K	p_c/MPa
Ethanol	>0.997	Guangfu	513.96	6.141	514.0 ± 7.0	6.30 ± 0.40
2-Propanol	>0.995	Guangfu	508.26	4.763	509.0 ± 2.0	4.90 ± 0.50
Cyclohexane	>0.990	Guangfu	553.61	4.074	554.0 ± 1.0	4.07 ± 0.05
Octane[b]	>0.990	Guangfu	568.92	2.496	568.90 ± 0.5	2.49 ± 0.01
Decane[b]	>0.990	Guangfu	617.73	2.106	617.80 ± 0.7	2.11 ± 0.08

[a] Standard uncertainties $u(T_c) = \pm 0.4$ K, and $u(p_c) = \pm 0.01$ MPa.
[b] Critical properties measured in our previous work [26].

critical pressures of three pure compounds (ethanol, 2-propanol and cyclohexane), four binary mixtures (ethanol + cyclohexane, ethanol + octane, 2-propanol + octane and 2-propanol + decane) and two ternary mixtures (ethanol + cyclohexane + octane and 2-propanol + octane + decane) are measured in this work. Some critical properties for ethanol + cyclohexane [21], ethanol + octane [22,23] and 2-propanol +octane [23,24] have been reported, but the experimental data in this work are in more detail and cover the full concentration range of the systems. The critical properties of the 2-propanol + decane system and two ternary systems are reported for the first time. The pure compounds, binary and ternary mixtures measured in this work are all thermally stable.

2. Materials and methods

2.1. Materials

Compounds used in this work were purchased from commercial sources. Details of compounds and the supplier are listed in Table 1. The purities of all compounds were above 0.99 and directly used without any further purification.

2.2. Apparatus

A flow view-type apparatus was designed in our previous work [26] to determine the critical properties based on the works of Roess [27] and Rosenthal and Teja [10]. Compared to the classical apparatus presented by Rosenthal and Teja, this apparatus adopts a quartz glass tube as the cell for visual observation, which makes the heating of the reagent more uniform. This apparatus can be operated up to 773 K for temperature and 10 MPa for pressure. The temperature of the system is measured by a temperature sensor (Fluke 5608-12 PRT, measurement uncertainty: ±0.02 K). The temperature sensor was inserted into the glass tube directly. Dual piston pump (LabAlliance 1500, flow control: 0.001 ml/min) and counterbalance valve are used to control the pressure of flow path, and the pressure of the system is measured by a pressure transducer (Rosemount 3051S; 0–10 MPa, accuracy: ±0.025%). An electric heating furnace was designed for the outside of the cell. The heaters were cast into the thermal insulation cavity which was filled with silica fiber particles, so the heating uniformity would be improved further. A temperature controller (Shimaden FP23, PID: 0.1) was used with auto-tuning settings. All sensor signals were collected by a digital multimeter (Keithley, 2002) and sent into computer by GPIB interface. Compound mass was measured with a high-precision electronic (Mettler Toledo ME204, 0.1 mg). A detailed description of the apparatus and experimental procedure are given in previous work [26], and the reliability of the apparatus was checked by measuring the critical properties of five pure alkanes and the ten binary alkane systems.

Table 2
Experimental uncertainties of temperature, pressure, and mole fraction.

	Factor of uncertainty	Uncertainty
Temperature	PRT, u_1	0.02 K
	Temperature measurement circuit, u_2	0.001 K
	Temperature control system, u_3	0.005 K
	Measurement repeatability, u_{rep}	0.2 K
	Combined uncertainty, u_c	0.2 K
Pressure	Pressure transducer, u_1	1.25 kPa
	Pressure measurement circuit, u_2	0.2 kPa
	Pressure control system, u_3	0.8 kPa
	Measurement repeatability, u_{rep}	5 kPa
	Combined uncertainty, u_c	5.2 kPa
Mole fraction	Mol number of first component, u_1	<0.0001
	Mol number of second component, u_2	<0.0001
	Mol number of third component, u_3	<0.0001
	Purity, u_p	<0.006
	Combined uncertainty, u_c	0.006

2.3. Assessment of uncertainties

The expanded uncertainties of temperature, pressure and mole fraction can be given by [28]:

$$U = k \cdot u_c = k\sqrt{\sum (u_i)^2} \quad (1)$$

where u_i is the uncertainty of each influencing factor, u_c is the combined standard uncertainty composed by each uncertainty of influencing factor, k is the 95% confidence coefficient that has a value of 2.

The mole fraction x is calculated by:

$$x_i = \frac{n_i}{n_1 + n_2 + \cdots + n_j} \quad (2)$$

where n_i is the mole number of component i, j was set to a value of 2 for binary systems and 3 for ternary systems. The expanded uncertainty of mole fraction is given by:

$$U_x = k \cdot u_c = k\sqrt{\left(\frac{\partial x}{\partial n_1}\right)^2 u_{n_1}^2 + \left(\frac{\partial x}{\partial n_2}\right)^2 u_{n_2}^2 + \cdots + \left(\frac{\partial x}{\partial n_i}\right)^2 u_{n_i}^2 + u_p^2} \quad (3)$$

where u_{n_1}, u_{n_2}, and u_{n_i} are the uncertainties of n_1, n_2, and n_i, i was set to a value of 2 for binary systems and 3 for ternary systems, u_p is the uncertainty caused by chemical purity. The maximum expanded uncertainties of temperature and pressure in this work are estimated to be less than ±0.4 K and ±0.01 MPa as shown in Table 2. Since the uncertainties of n_i are small, the expanded uncertainty of mole fraction is estimated to be less than ±0.012 for both binary systems and ternary systems.