J. Chem. Thermodynamics 111 (2017) 265–270

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

Heat capacity of isobutane in liquid phase at temperatures from 303 K to 413 K and pressures up to 12 MPa

Yu Liu, Xiaoming Zhao *, Shaohua Lv

MOE Key Laboratory of Thermo-Fluid Science and Engineering, Xi'an Jiaotong University, Xi'an, Shaanxi 710049, China

ARTICLE INFO

Article history:
Received 19 September 2016
Received in revised form 14 March 2017
Accepted 28 March 2017
Available online 30 March 2017

Keywords:
Heat capacity
Isobutane
Liquid
Flow calorimeter

ABSTRACT

The measurements of isobaric heat capacity for isobutane were carried out using a flow calorimeter in both compressed liquid and supercritical phase. 250 data of heat capacity were obtained at the temperature range from 303 K to 413 K at pressures up to 12 MPa. The relatively expanded uncertainty in the heat capacity measurement was estimated to be less than 1% with $k = 2$ (95%). An empirical equation was correlated to represent the experimental values with an average absolute deviation of 0.7%. In addition, the saturated liquid heat capacities of isobutane were also derived by extrapolating the empirical equation to the corresponding saturated pressure.

1. Introduction

Isobutane is an important hydrocarbon substance. It is widely used in a great deal of engineering applications, especially the refrigerator industry as an environmentally friendly alternative for its many valuable advantages, such as zero ozone depletion potential and a very low global warming potential, large volumetric cooling capacity and high COP (coefficient of performance) [1,2]. Although the flammability of isobutane limits its use as a refrigerant, the appropriate improvement in refrigeration system makes it an attractive working fluid in refrigerator industry.

The research about the thermophysical properties of isobutane is essential for its engineering applications. Various properties for isobutane have been studied before. Such as vapor pressure [3], critical point [4], PVT properties [5], surface tension [6], thermal conductivity [7], viscosity [8]. As for the isobaric heat capacity of isobutane, the experimental data are still very limited, especially in the compressed liquid phase. Sage et al. [9] investigated isobaric heat capacities of isobutane at temperatures from (294 to 394) K in gaseous and saturated liquid phase. Parks et al. [10] measured its isobaric heat capacities at temperatures from (79 to 261) K. Aston et al. [11] studied the heat capacity of isobutane over a temperature range from 12 K to the normal boiling point. Dailey and Felsing [12] measured gaseous heat capacities with a calorimeter from (347 to 692) K. Wacker et al. [13] measured isobaric heat capacities in a temperature range from (243 to 353) K in vapor phase. The most recent measurements for the heat capacity of isobutane in vapor phase were carried out by Ernst and Busser [14] in 1970 over the temperature range of (293 to 353) K with corresponding pressures up to 0.8 MPa. To the author's knowledge, the isobaric heat capacities for isobutane in compressed liquid phase have not been reported until now.

In this work, the heat capacity of isobutane in compressed liquid and supercritical phase was investigated by means of a modified flow calorimeter, a total of 250 data points were acquired at temperatures from 303 K to 413 K and pressures from 1.0 MPa to 12 MPa.

2. Experimental

2.1. Chemicals

The sample of isobutane used in this work was provided by Zhejiang Sinoloong refrigerant Co. Ltd. The mass fraction purity stated by the manufacturer is greater than 99.95%. No further purification was performed before use. The detailed information of the sample used in this paper was shown in Table 1.

2.2. Experimental method

The isobaric heat capacity of a fluid can be calculated by [15,16]

$$c_{p,app} = Q/(m \cdot \Delta T) \tag{1}$$

where Q refers to the heat flux received from the heater, m is the mass flow rate, ΔT represents the temperature rise of the sample

---

* Corresponding author.
E-mail address: xmzhao@mail.xjtu.edu.cn (X. Zhao).

http://dx.doi.org/10.1016/j.jct.2017.03.033

Table 1
Source and purity of the experimental substance.

Chemical name	Source	Mass fraction purity	Purification method
Isobutane	Zhejiang Sinoloong refrigerant co.Ltd.	0.9995	None

after receiving a heat flux. Note that the heat flux Q consists of the heat absorbed by the fluid and heat loss from the calorimeter to the surroundings. Therefore, the real heat capacity can be calculated by

$$c_{p,app} = Q/(m \cdot \Delta T) = (Q_F + Q_L)/(m \cdot \Delta T) = c_p + Q_L/(m \cdot \Delta T) \qquad (2)$$

where $c_{\boldsymbol{p},\ \boldsymbol{app}}$ describes the observed isobaric heat capacity, $Q_L$is the heat loss of the heater. From Eq. (2), it can be seen that the effect of the heat loss upon the heat capacity fell as mass flow rate m rose. In this case, the impact of the heat loss can be determined by measuring the heat capacity at different mass flow rate and extrapolating m to infinite flow. As shown in Eq. (2), the influence of heat leak should vanish, $c_{\boldsymbol{p},\ \boldsymbol{app}}$ can be viewed as c_p when 1/m is zero. Note that $T = (T_1 + T_2)/2$. Here, T_1 and T_2 are the temperatures at the inlet and outlet of the calorimeter.

2.3. Apparatus

The detailed description of isobaric heat capacity measurement system was introduced in our former work [17]. In this section, the experimental system is introduced concisely. The isobaric heat capacity system applied in this study mainly included a calorimeter, a mass flowmeter, a thermostatic bath, a temperature measurement system and a pressure measurement system. Among them, the calorimeter is the key part. It consists of two standard platinum resistance thermometers, a microheater and a stainless steel cell. The heater is inserted into a specially designed structure.

As illustrated in Fig. 1, the sample fluid was driven by a constant-flux pump, which could deliver the fluid at a given flow rate. The sample flows through a long winding stainless steel tube placed in a thermostatic bath to make sure that the sample reaches the thermostatic bath temperature before it enters the calorimeter. Then the sample flows into the calorimeter and is heated evenly at the same time in a narrow annular channel. The sample temperatures at the inlet and outlet of the calorimeter are acquired with two standard platinum resistance thermometer. The pressure is obtained directly by a pressure sensor. In addition, the mass flow rate is measured by a mass flow meter (SIEMENS, MASS 2100, DI1.5). According to Eq. (1), the isobaric heat capacity can be obtained by measuring the temperature increment and the heat flux and the mass flow rate.

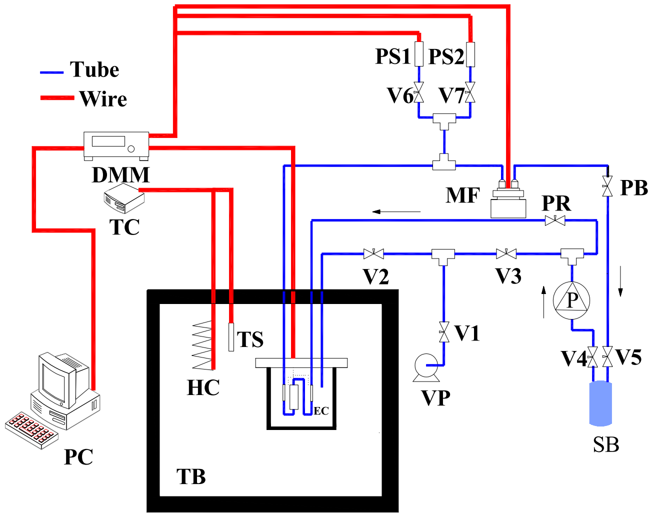

Fig. 1. Schematic diagram of the experiment system: TB, Thermostatic bath; EC, Experimental cell; TS, Thermometer; HC, Heater; TC, High accuracy temperature controller; DMM, Keithley 2700 data acquisition system; PC, Computer; PS1,PS2, Pressure sensor; MF, Siemens mass flowmeter; VP, Vacuum pump; SB, Sample bottle; V1-V7, Needle valve; PR, Pressure reducing valve; PB, Back pressure valve; P, Constant-flux pump.

2.4. Assessment of uncertainties

The uncertainties of our experimental system in this work are listed as follows. The temperature measurement system consists of a multimeter (keithley 2700 data acquisition system) and two standard platinum resistance thermometers. The standard combined uncertainty of temperature for the isobaric heat capacity was within 10 mk. The standard combined uncertainty of pressure measurement is estimated to be less than 15 kPa. The mass flow rate is a very important property in this study due to its significant impact on the calculation of the heat capacity. The mass flow rate in this experiment should always be set to be greater than 5% of the maximum value to ensure that the measurement uncertainty of the mass flow rate is less than 0.05%.The microheater that supplied heat flux is controlled by the direct current. The voltage and current could be measured by a multimeter. Therefore the standard combined uncertainty of the heat flux is determined to be less than 0.01%.

According to the propagation law of uncertainty, the relatively expanded uncertainty of isobaric heat capacity in this paper could be concluded by Eq. (3).

$$U_{c,c_p} = k\sqrt{(\delta Q/Q)^2 + (\delta T/T)^2 + (\delta m/m)^2} \qquad (3)$$

Here, $k$is coverage factor with a value of 2. $\delta Q/Q$, $\delta T/T$, $\delta m/m$ are uncertainties caused by heat power, temperature rise and flow rate. The relatively combined uncertainty of the isobaric heat capacity is estimated to be less than 1.0% at temperatures below 403 K. In the near critical region (403 K and 413 K), the combined uncertainty of the heat capacity is evaluated to be 2%.

3. Results and discussions

250 data points in compressed liquid and supercritical phase were acquired for isobutane at temperatures from 303 K to 413 K and pressures from 1.0 MPa to 12 MPa. Results of the measurements are given in Table 2, as illustrated graphically in Fig. 2. As shown in Fig. 2 and Fig. 3, the isobaric heat capacity drops marginally as pressure increases. Nevertheless, the heat capacity of isobutane goes up when the temperature rises. Moreover, when the temperature is lower than 373.92 K (including 373.92 K), the value of heat capacity decreases slowly as pressure increases. However, when temperature is higher than 373.92 K, the influence of pressure is greater, the isobaric heat capacity of isobutane falls quickly as pressure increases. Temperature has a great effect on the heat capacity value, an increase of 20 K in temperature leads to a rise of around (3–138)% in the heat capacity. Furthermore, the effect of temperature is stronger as temperature increases. For example, the heat capacity at $P = 4.0$ MPa for isobutane rises by 2.9% in the temperature range from 303 K to 323 K and increases by more than 138% at temperatures from 403 K to 413 K. The effect of pressure on heat capacities should be taken into account. As can be seen, the heat capacity at lowest pressure is always the peak-point at each isotherm. The difference in the isobaric heat capacity between lowest-pressure and $P = 12$ MPa is about (6–250)% when temperature remains constant. The influence of pressure increases as tem-