Fluid Phase Equilibria 418 (2016) 125–132

Contents lists available at ScienceDirect

Fluid Phase Equilibria

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

Measurements of the speed of sound in liquid and supercritical ethane

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ARTICLE INFO

Article history:
Received 1 September 2015
Received in revised form
12 November 2015
Accepted 17 November 2015
Available online 26 November 2015

Keywords:
Ethane
High pressure
Pulse-echo method
Speed of sound

ABSTRACT

Comprehensive and accurate measurements of the speed of sound in pure ethane have been carried out in the liquid and supercritical regions by a double-path-length pulse-echo technique. The measured data cover the temperature range from 240 K to 420 K with pressures up to 100 MPa. The expanded measurement uncertainties at the 95% confidence level amount to 2.1 mK for temperature, 0.007% for pressure, and 0.01% for speed of sound with the exception of a few state points in the vicinity of the critical point, where the uncertainty increases up to 0.016%. The quality of the measurements is demonstrated by comparisons with literature data and the fundamental equation of state for ethane by D. Bücker and W. Wagner [J. Phys. Chem. Ref. Data 35 (2006) 205–266].

1. Introduction

Ethane is an important fluid with many industrial and scientific applications. For example, it is one of the most important basic substances in many production processes in the chemical industry, and it occurs as the second main component in natural gas beside methane. Moreover, it often serves as a reference fluid for developing equations of state or is used for validating models of intermolecular forces in molecular simulations. Therefore, precise knowledge of its thermodynamic properties is desirable.

Thermodynamic properties of a fluid are best represented by fundamental equations of state, from which all thermodynamic properties can be calculated. For developing and optimizing fundamental equations of state accurate speed-of-sound data sets in the liquid phase are very useful. They contribute to improving the description of the liquid region, the extrapolation behavior and the representation of caloric properties. For ethane, the most accurate fundamental equation of state was published by Bücker and Wagner [1]. For the optimization of the equation of state in the liquid phase, only one comprehensive speed-of-sound data set by Tsumura and Straty [2] was available. These data were measured with a sing-around pulse-echo technique, have an uncertainty of 0.05% and cover the low temperature range between 100 K and 323 K with pressures up to 37 MPa. Besides, Trusler and Costa Gomez [3] measured a few data with a spherical resonator on the supercritical isotherm 350 K up to 20 MPa. At low pressures in the liquid phase, the Bücker and Wagner equation of state describes the speed of sound with an uncertainty of 0.15%. At pressures above 40 MPa the uncertainties increase to 1% up to 100 MPa, and even reach 5% at higher pressures. With our speed-of-sound instrument [4,5] very accurate speed-of-sound data with uncertainties well below 0.05% were already measured for several pure fluids, e.g. Refs. [6,7]. Thus, the aim of this work was to extend the measurement range for the speed of sound in liquid and supercritical ethane to higher pressures up to 100 MPa and higher temperatures up to 420 K. The new data can subsequently be used to improve the formulation of the Helmholtz energy for ethane.

2. Experimental procedure

Our speed-of-sound instrument, the calibration procedure, and the analysis of measurements have been described in detail in Refs. [4,5]. The measurement principle of our speed-of-sound sensor is based on a double-path-length pulse-echo technique, which was first introduced by Muringer et al. [8]. A piezoelectric quartz crystal with a resonance frequency of 8 MHz is employed as a sound emitter and receiver. In the analysis of the speed-of-sound measurements, corrections for changes of the distances in the sensor with temperature, for compression of the sensor with pressure, and for diffraction effects are applied as described in Ref. [4].

The speed-of-sound sensor is housed in a pressure vessel, which is thermostated in a circulating liquid-bath thermostat. The temperature inside the pressure vessel is kept constant within 0.5 mK during the course of one measurement. The temperature was measured by a 25-Ohm standard platinum resistance thermometer

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http://dx.doi.org/10.1016/j.fluid.2015.11.019
0378-3812/

in the wall of the pressure vessel. The thermometer was calibrated on the ITS-90, and the uncertainty of the temperature measurement is estimated to be 2.1 mK. The resistance of the thermometer was measured with an ASL-F18 bridge system with calibrated reference resistors. The pressure inside the pressure vessel was measured with a nitrogen-operated gas pressure balance. The pressure balance was coupled to the sample liquid via a differential pressure null indicator (Ruska membrane type cell). The uncertainty of the pressure measurement is less than 70 ppm. Both temperature and pressure measurement uncertainties are for a 95% confidence level.

The acoustic path length $\Delta l = 2(l_2 - l_1)$ at zero pressure and 273.15 K and the temperature dependent thermal expansion coefficient of the sensor material were determined by calibration measurements in gaseous argon at pressures between 10 MPa and 13 MPa and temperatures between 240 K and 420 K. Argon was used as a calibration fluid instead of water because it enables to calibrate the sensor in a wider temperature range and to achieve a lower uncertainty of the calibration. With the speed-of-sound data of Estrada-Alexanders and Trusler [9], which have a relative uncertainty of 10 ppm, accurate references for the speed of sound in argon are available. The analysis of the calibration measurements was started with a calibration function from a previous measurement campaign. Minimization of the deviations of our measurements from the reference data of Estrada-Alexanders and Trusler was achieved by reducing the value of the acoustic path length at zero pressure and 273.15 K by about 0.014%. The difference to the previous calibration is probably due to the fact that the sensor was disassembled and reassembled before the calibration measurements. After the calibration two complete measurement campaigns with different ethane samples were carried out. These measurements had to be discarded because the samples were contaminated with air. Then the present ethane measurements were conducted, followed by a second calibration with argon which was also carried out and analyzed as described above. It was found that the acoustic path length had increased by 0.035% since the first calibration. It is assumed that this difference is due to small movements of the crystal in the speed-of-sound sensor during temperature and pressure cycles. To check the reproducibility of the speed of sound after the second calibration, a few measurements at $T = 340$ K were repeated since this isotherm was measured first. These data deviated from the speeds of sound of the main measurement campaign by up to 55 ppm when evaluated with the same calibration function for the acoustic path length. This result provided high confidence that the speed-of-sound measurements for ethane are very consistent and are not affected by the rather large difference between the two calibrations. For this reason the ethane measurements were evaluated with the second calibration, and an additional allowance of 55 ppm was added as a systematic contribution to the combined uncertainty of the speed of sound. The observed difference of 55 ppm is probably also due to movements of the crystal during frequent temperature changes in the second calibration.

Fig. 1 shows the deviations of our second series of calibration measurements and of the data of Estrada-Alexanders and Trusler from the accurate fundamental equation of state of Tegeler et al. for argon as a function of temperature after adjustment of the acoustic path length. Our measurements agree with the data of Estrada-Alexanders and Trusler within 20 ppm with the exception of two points, which deviate by 35 ppm and 45 ppm from the data of Estrada-Alexanders and Trusler. These two points were discarded in the analysis of the calibration measurements. Their deviations are covered by the additional allowance of 55 ppm to the uncertainty of the speed of sound described above. The expanded uncertainty (confidence level 95%) of the determination of the

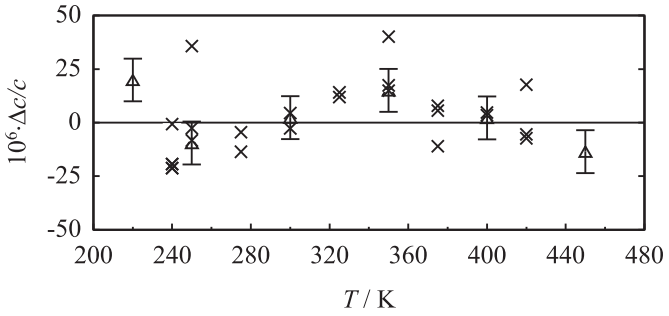

Fig. 1. Relative deviations of measured speeds of sound in gaseous argon from the fundamental equation of state of Tegeler et al. after adjustment of the acoustic path length. Legend: ×, This work; △, Estrada-Alexanders and Trusler.

acoustic path length is estimated to be 40 ppm. It includes contributions from the time, temperature and pressure measurements, the uncertainty of the reference data, the deviation of the calibration measurements from the reference data, and the correction of the acoustic path length to zero pressure. Estrada-Alexanders and Trusler did not state whether the reported uncertainty of their speed of sound data is at the 68% or 95% confidence level. In our uncertainty analysis, it was considered as an expanded uncertainty at the 95% confidence level. A detailed summary of all contributions to the measurement uncertainties is given in Table 1.

For the measurements in ethane, the resolution of the time measurements is less than 2 ppm, while the reproducibility of the speed of sound after temperature and pressure cycles during the measurement campaign is less than 25 ppm, at high pressures it is even less than 10 ppm. It is assumed that the reproducibility of the time measurements is limited by the reproducibility with which the temperature and pressure of a state point can be set in the pressure vessel. The uncertainty of the speed-of-sound measurement is 45 ppm at the 95% confidence level, excluding contributions from sample impurities, from temperature and pressure measurement uncertainties and from the reproducibility after the second calibration.

The ethane sample was purchased from Westfalen, Germany, had a manufacturer specified volume purity better than 99.999% and was used as delivered. According to the manufacturer's specification the volume purity is as follows: other hydrocarbons (CH_4, C_2H_4, C_2H_2, C_3H_8, and C_{4+}): ≤6 ppm, nitrogen: ≤3 ppm, carbon dioxide: ≤2 ppm, oxygen: ≤1 ppm, and water: ≤1 ppm. To account for sample impurities, an additional allowance of 10 ppm was added to the combined uncertainty of the speed of sound.

3. Results

Our measurements cover the liquid and supercritical region between $T = 240$ K and $T = 420$ K with pressures up to 100 MPa and were conducted along 10 isotherms in steps of 20 K. Additionally, measurements on the critical isotherm at $T_{crit} = 305.32$ K were carried out. In order to compare our measurements with the spherical resonator data of Trusler and Costa Gomez, some data were measured between 13 MPa and 25 MPa at $T = 350$ K. On subcritical isotherms the lowest pressure was chosen slightly above the vapor pressure of ethane at ambient temperature of about 3.75 MPa, while on supercritical isotherms measurements were started at the lowest pressure where a clear signal cancellation could be observed on the oscilloscope. The measurement results are listed in Table 2. Our speed-of-sound data on the eleven completely measured isotherms are shown in Fig. 2 as a function of pressure. In the region of our measurements, the speed of sound ranges from 310 ms^{-1} to 1620 ms^{-1}.