



Density and speed of sound measurements of 1- and 2-butanol[☆]

Stephanie L. Outcalt^{*}, Arno Laesecke, Tara J. Fortin

Thermophysical Properties Division, Chemical Science and Technology Laboratory, National Institute of Standards and Technology, 325 Broadway, Boulder, CO 80305-3337, USA

ARTICLE INFO

Article history:

Received 9 September 2009

Received in revised form 4 November 2009

Accepted 7 November 2009

Available online 12 November 2009

Keywords:

Adiabatic compressibility

Biofuels

1-butanol

2-butanol

Compressed liquid

Density

Speed of sound

ABSTRACT

The density and speed of sound of 1- and 2-butanol have been measured with two instruments; both instruments used vibrating-tube sensors for measuring density. At ambient pressure (83 kPa), density and speed of sound were measured from 278.15 K to 343.15 K. Adiabatic compressibilities were derived from these density and speed of sound data. Compressed liquid density measurements were carried out in a second instrument over a range from 270 K to 470 K with pressures from 0.5 MPa to 50 MPa. The measured density data were correlated with a modified Tait equation within their experimental uncertainty, and this correlation provides a baseline for extensive comparisons with literature data. Differences between the measured macroscopic properties of the two butanol isomers are related to differences on the molecular level. These were characterized by quantum mechanical calculations using the second-order Møller–Plesset model with the polarization basis set 6-311+G**.

Published by Elsevier B.V.

1. Introduction

This contribution is part of a series of measurements, the goal of which is to systematically characterize the thermophysical properties of fuels and their constituents over wide ranges of temperature and pressure. While previous reports have communicated measurement results for jet fuels [1], rocket fuels [2], and their constituents methyl- and propylcyclohexane [3] and hexadecane [4], two butanol isomers (1- and 2-butanol) have been characterized in this work.

There are four isomers of the aliphatic alcohol with the molecular formula C₄H₉OH. One of the two isomers with a primary hydroxyl group is 1-butanol or *n*-butanol (CAS no. 71-36-3). The only isomer with a secondary alcohol group at an internal carbon atom is 2-butanol (CAS no. 78-92-2), also known as *sec*-butanol, 2-butyl alcohol, or 1-methyl-1-propanol. The other isomer with a primary hydroxyl group is 2-methyl-1-propanol, and the isomer with a tertiary hydroxyl group is 1,1-dimethyl-ethanol or 2-methyl-2-propanol.

Interest in butanols as a second-generation biofuel has increased in recent years because they have many advantages over other potential alternative fuel candidates such as ethanol. At 85% by volume with gasoline, butanols can be used in cars designed for gasoline without requiring any retrofit to the engine (unlike 85% ethanol, E85) [5]. They have a higher energy content for a given volume than

ethanol, and almost as much as gasoline. Butanols can also be used as a blended additive to gasoline to reduce carbon monoxide emissions [6], and are less susceptible to separation in the presence of water than ethanol/gasoline blends, therefore allowing use of the industry's existing distribution infrastructure without requiring modifications to blending facilities, storage tanks or retail station pumps [5].

Despite the advantages butanols may provide as an alternative fuel, there are still significant gaps in the thermophysical properties data, particularly for 2-butanol. Also, there is a fair amount of scatter in the data for both 1- and 2-butanol. The measurements reported here were undertaken to provide data where none exist, and to help resolve some of the differences between published data sets.

Results of density and speed of sound measurements for 1- and 2-butanol are reported in this work. Adiabatic compressibilities have been derived from the ambient pressure density and speed of sound data and are also included. Compressed liquid density data have been extrapolated to saturation pressure and combined with ambient pressure density data for correlation with a Rackett equation. Additionally, the compressed liquid density data have been correlated with a modified Tait equation and compared to existing literature data.

2. Molecular characterization

A major goal of our research is to provide accurate macroscopic thermophysical properties data and to relate them to the molecular

[☆] Contribution of the National Institute of Standards and Technology. Not subject to Copyright[©] in the USA.

^{*} Corresponding author. Tel.: +1 303 497 5786; fax: +1 303 497 5224.

E-mail address: Outcalt@Boulder.NIST.Gov (S.L. Outcalt).

size, shape, and charge distribution of the measured compounds. The isomers 1- and 2-butanol were chosen for the measurements reported in this work to elucidate how the change of the hydroxyl group from a primary to a secondary position on the molecular level is reflected in the densities and speeds of sound of the two compounds over a wide range of temperature and pressure. Measurements over wide temperature ranges provide particularly detailed insight into the effects of electrostatic attractions between polar molecules such as alcohols that associate with each other and form hydrogen bonds. On the molecular level, our approach includes the computational characterization of the test compounds by *ab initio* calculations of their equilibrium geometries and charge distributions in the Møller–Plesset theory level MP2 with 6-311+G** basis sets [7]. The two molecules are compared in Fig. 1 in three views of their electron density isosurface at 0.002 electrons a.u.⁻³ (where 1 a.u. = 5.292 nm, the Bohr radius of hydrogen). The electrostatic potential is color-mapped onto the electron density isosurface indicating the charge distribution in the molecules [8]. The three views of the molecules, two frontal and one along the longitudinal axes, reveal differences in shape and polarity between the two isomers. They give an appreciation of the possible ordering of the molecules in condensed phases and the associated void volumes. While the calculated molecular volumes agree very well, the molecular surface area of 2-butanol is 2.4% smaller than that of 1-butanol. Visualizations of the molecular charge distributions as in Fig. 1 facilitate the understanding of structural effects due to electrostatic attractions and repulsions, which are prominent in polar molecules such as 1- and 2-butanol. At 1.7 debye, the calculated dipole moment of 2-butanol agrees with the same value reported in the compilation of Poling, Prausnitz, and

O'Connell [9]. In contrast, at 1.74 debye, the calculated dipole moment of 1-butanol is 2.4% lower than the reported value of 1.8 debye [9]. The work reported here illustrates how these characteristics on the molecular level are reflected in the measured macroscopic properties density and speed of sound.

3. Experimental

The 1- and 2-butanol samples measured in this work were obtained from Sigma-Aldrich Chemicals¹ both with a stated minimum purity of 99.5%. Because of their hygroscopicity, activated molecular sieves type 5A, grade 521, with an effective pore size of 5 Å were added to each of the sample bottles to keep the butanols dry of contamination from ambient humidity. Karl Fischer analysis performed on each of the samples prior to measurements determined the water content to be just at the detection limit of approximately 20 ppm. Measurements at ambient pressure were conducted on the samples with no additional analysis or purification.

Prior to measurements of compressed liquid density, samples were transferred to stainless steel cylinders and degassed as described in Outcalt and McLinden [10]. The sample of 2-butanol used to charge the system for the compressed liquid density measurements was analyzed in our laboratory with a gas chromatographic method and found to be within manufacturer specifications. An analysis was also performed on the 2-butanol collected at the outlet of the instrument to determine whether thermal breakdown or any type of contamination took place during the measurements. No significant differences between fresh and used samples were detected.

A DSA 5000 analyzer from Anton Paar Company was used to measure density and speed of sound at ambient pressure. Details of the instrument and experimental procedures have been reported in Laesecke et al. [3]; thus, only a brief description is given here. The instrument contains a sound speed cell and a vibrating quartz tube densimeter in series. Temperature is measured with an integrated Pt-100 thermometer with an estimated uncertainty of 0.01 K. The instrument was adjusted with air and deionized water at 293.15, 313.15, and 333.15 K. In addition, the instrument performance is checked before and after measurements to ensure that the density and speed of sound of water at 293.15 K are reproduced within 100 ppm. For the 1- and 2-butanol measurements, temperature scans were programmed from 343.15 K to 278.15 K in 5 K increments. Fresh samples of test liquid were injected for each temperature scan instead of performing repetitive measurements on the same sample. At least four temperature scans were performed for both fluids. The relative standard deviation (reproducibility) of these repeated sound speed measurements was no greater than 0.07% and no more than 0.001% for density. Based on repeated measurements of the speed of sound of water, we conservatively estimate the uncertainty of our sound speed measurements to be 0.3% ($k=2.3$). To more accurately estimate the uncertainty of the ambient pressure density measurements, densities of NIST SRM 211d (toluene) were measured over the temperature range of the instrument and compared to the correlation of McLinden and Splett [11]. Based on these comparisons, we conservatively estimate the uncertainty of our ambient pressure density measurements to be 0.04% ($k=2.3$).

Densities of the compressed liquids were measured with the automated densimeter of Outcalt and McLinden, details of which have been described in a previous publication [10]. The core of the apparatus is a commercial vibrating-tube densimeter (DMA-HPM from Anton Paar Company) which is housed in a custom designed

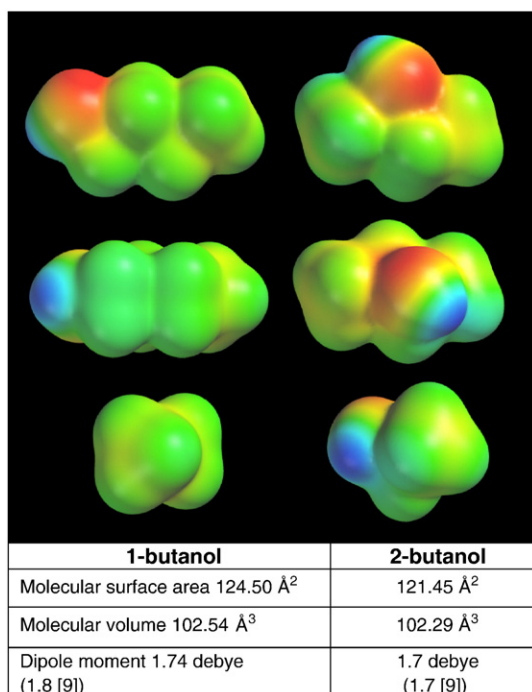


Fig. 1. Comparison of molecular size, shape, and charge distribution of 1- and 2-butanol. The electrostatic potential is color-mapped onto an electron density isosurface at the level of 0.002 electrons a.u.⁻³ (with 1 a.u. = 5.292 nm being the Bohr radius of hydrogen). This surface represents approximately 99% of a molecule. The color scale ranges from red (negative charge) to blue (positive charge). Each molecule is shown in two frontal views (top row and center row) and along the longitudinal axis (bottom row) to illustrate size and shape differences. Molecular data in the table are based on equilibrium geometry calculations at the MP2 theory level with 6-311+G** basis sets. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

¹ In order to describe materials and experimental procedures adequately, it is occasionally necessary to identify commercial products by manufacturers' names or labels. In no instance does such identification imply endorsement by the National Institute of Standards and Technology, nor does it imply that the particular product or equipment is necessarily the best available for the purpose.

Download English Version:

<https://daneshyari.com/en/article/5413036>

Download Persian Version:

<https://daneshyari.com/article/5413036>

[Daneshyari.com](https://daneshyari.com)