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Speed of sound measurement in ethyl tert-butyl ether and tert-amyl methyl ether by Brillouin light scattering

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ABSTRACT

Ethyl tert-butyl ether (ETBE) and tert-amyl methyl ether (TAME) have been considered as the potential fuel additives as the replacement of methyl tert-butyl ether (MTBE). Now it is necessary to supplement and perfect the thermophysical properties of oxygenates, including acoustic property. In this paper, speed of sound in ETBE and TAME were measured by Brillouin light scattering from 293.15 K to 680 K and from saturated vapor pressure to 10 MPa, including saturated liquid/vapor, compressed liquid and supercritical region. It is estimated that $u\ (T) = 0.01$ K under saturated condition; $u\ (T) = 0.02$ K, $u\ (p) = 0.015$ MPa for $p < 5.5$ MPa, $u\ (p) = 0.03$ MPa for $p > 5.5$ MPa under compressed liquid and supercritical conditions; and the relative expended uncertainty in the speed of sound is estimated to be less than 0.5% with coverage factor of k to be 2. Moreover, the reference relations of the speed of sound for saturated liquid, vapor and compressed state are presented for interpolation with the average absolute deviation of 0.23%, 0.07% and 0.33% for ETBE and 0.34%, 0.24% and 0.29% for TAME, respectively.

1. Introduction

In order to improve the performance of gasoline, additives are always added into the gasoline. The effect of the gasoline additives is to reduce the levels of mainly soot and particulate emissions and to improve combustion. In 1920s, tetraethyl lead (TEL) was found to be a good fuel additive, and then it was used worldwide. While it was found to be harmful to environment and human body, TEL was gradually being banned as fuel additive [1]. Nowadays, because of the high oxygen amount and octane rating, ethers have become important gasoline additives. They could be used to reduce emissions and the contaminant agents of automobile catalysis. Methyl tert-butyl ether, MTBE, is the most widely used gasoline additive. However because of its high water solubility, it has been outlawed in many countries recently [2]. So it is important to look for the alternatives of MTBE as the gasoline additive. Ethyl tert-butyl ether (ETBE) and tert-amyl methyl ether (TAME) were suggested as the potential alternatives of MTBE [3].

Speed of sound is a basic thermophysical property. And it is also used to obtain other derived thermodynamic properties like isentropic and isothermal compressibility, isobaric thermal expansion coefficient, thermal pressure coefficient and the reduced bulk modulus [4,5].

Acoustic method is a traditional method researched by many authors [6–9]. Two types of resonators are used in this method, one is spherical resonator, the other is cylinder resonator, and each method has their own characteristics. For spherical resonator, the measurement precision of is high while the resonator is hard to manufacture. For cylinder resonator, the quality factor is lower while the resonator is easier to manufacture and assemble. In these years, Brillouin light scattering (BLS) method has been regarded as a promising method for the measurement of the speed of sound. Some researchers have measured the speed of sound of many organic fluids using this method, such as R227ea [10], R365mfc [11], toluene [12], etc.

The speed of sound measurements in ETBE and TAME are very scant, and the available experimental data in literature are focused on the low T-p region. R. Gonzalez-Olmos et al. measured the speed of sound of ETBE and TAME at the atmospheric pressure and the temperature ranging from (278.15 to 323.15) K [13]. And there are also other measurements of speed of sound in ETBE and TAME for binary system or ternary system [14,15]. So, in order to supply more new experimental data, the speed of sound of ETBE and TAME in a wide T-p region were measured using BLS method.

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2. Experimental section

2.1. Material

The ETBE and TAME samples were provided by Aladdin Reagent Inc. with specified mass purity higher than 0.990 (GC). The samples were not further purified in order to prevent samples alterations. The specifications of the samples are listed in Table 1. Because dust and particles could influence the measurement, so the samples were filtered through membrane filters with 0.22 μm pure size when filling the sample cell in order to prevent dust and particles from entering the cell.

2.2. Measurement principle

Brillouin light scattering method was used to measure the speed of sound in this work. Here the fundamental principle is presented as follows.

When BLS method is used to measure the speed of sound, the Brillouin components in the spectrum of the scattering light should be investigated. The spectrum is shown as Fig. 1, which is composed of three peaks, central Rayleigh peak, Brillouin peak and anti-Brillouin peak, Brillouin peak and anti-Brillouin peak are symmetrical respected to Rayleigh peak. And the speed of sound of fluids is related to the frequency shift between Brillouin peak and Rayleigh peak, the relationship is shown as Eq. (1),

$$c = \frac{\Delta\omega}{q} \tag{1}$$

where c is the speed of sound, $\Delta\omega$ is the frequency shift of the Brillouin peak and q is the modulus of scattering vector.

According to Bragg's law, the modulus of scattering vector can be calculate using Eq. (2),

$$q = \frac{4n\pi \sin(\theta/2)}{\lambda_0} \tag{2}$$

where θ is the scattering angle, n is the refractive index and λ_0 is the wavelength of the incident light in vacuum. According to the refractive law, when scattering angle is small enough, Eq. (2) could be converted into the following equation:

$$q = \frac{2\pi \sin\Theta_{ex}}{\lambda_0} \tag{3}$$

where Θ_{ex} is the incident angle in the air. The value of q is a parameter when we use a certain laser irradiates the fluid in a certain angle. So, if the spectrum of the scattering light is gotten, the frequency shift and the speed of sound of the fluid could be gotten.

2.3. Experimental apparatus

The experimental setup is shown in Fig. 2. A continuous wave diode pumped solid state laser (Cobolt Samba™, 532 nm, 300 mW) with a single longitudinal mode is used to supply laser source. And before the laser beam irradiates the sample, a Glan–Taylor prism is used to improve the polarization of the laser beam. And then, the laser beam irradiates the sample and induces it producing the scattering light. And the scattering light is filtered by Fabry–Perot interferometer (FPI, Thorlabs SA200-5B), and the photon counting head (Hamamatsu H8259-01) is used to detect the scattering light and convert it into TTL single. And the TTL single is recorded by a data acquisition card (DAQ card, NI-PCI6221). In the end, we can get the spectrum of the scattering light in our PC.

The temperature, the pressure control, and the measurement units in the present research are shown in Fig. 3. In the system, a secondary standard platinum resistance thermometer (SPRT, Fluke 5608-12) is used to measure the temperature, and a pressure transmitter (Rosemount 3051s) is used to measure the pressure. The temperature measurement uncertainty is less than 10 mK in saturated state and 20 mK in compressed liquid and supercritical region. The pressure measurement uncertainty is less than 0.015 MPa for $p < 5.5$ MPa and 0.03 MPa for $p > 5.5$ MPa.

The principle and experimental setup of this method was described in detail in our previous paper and in various fundamental studies [16–20].

Table 2
Comparison of speed of sound of saturated liquid toluene with the data calculated with EOS.[a]

T (K)	p (MPa)	$c^{\text{This work}}$ (m s^{-1})	c^{Lemmon} (m s^{-1})	c^{Will} (m s^{-1})
303.15	0.00	1200.8	1198.0	1195.1
353.15	0.04	1000.0	1000.4	992.4
413.15	0.22	806.0	810.8	798.8
463.15	0.63	616.2	621.4	612.3
523.15	1.67	425.5	422.5	420.6

[a] The standard uncertainty u is u (T) = 0.01 K and the relative expanded uncertainty U_r is U_r (c) = 0.005 (0.95 level of confidence).

2.4. Assessment of experimental uncertainties

The relative combined variance in the speed of sound can be estimated by Eq. (4),

$$u_r^2(c_s) = 0.0015^2 + u_r^2(\Delta\omega) + u_r^2(\lambda_0) + (-1)^2 u_r^2(\Theta_{ex}) \tag{4}$$

where u_r ($\Delta\omega$), u_r (λ_0), and u_r (Θ_{ex}) are the relative standard uncertainties due to the Brillouin frequency shift, the wavelength of the incident light, and the incident angle, respectively. Constant 0.0015 results from the approximate calculation of the modulus scattering vector. The relative standard uncertainty caused by spectrum measurement, wavelength stability and scattering angle measurement are 0.002, 3.76×10^{-5} and 1×10^{-3}, respectively. Substituting the four uncertainty components into Eq. (4), the relative combined uncertainty u_r (c) = 0.0025 is obtained. Finally, the relative combined expanded uncertainty ($Ur = ku_r$) of 0.005 with a coverage factor of $k = 2$ with 0.95 level of confidence is estimated for the speed of sound.

A more detailed description of the measurement uncertainties

Table 1
Specifications of the chemical samples in this study.

Chemical name	Source	Initial mass fraction purity	Purification method	Final mass fraction purity	Analysis method
ETBE	Aladdin Reagent Inc.	>99.0%	Filtered through a membrane filter	–	–
TAME	Aladdin Reagent Inc.	>99.0%	Filtered through a membrane filter	–	–
Toluene	Tianjin Baishi Chem. Eng. Co. Ltd.	>99.5%	Filtered through a membrane filter[a]	–	–

[a] When filled into the sample cell, the samples were filtered through the membrane filter with 0.22 μm pore size.