Evaluation of glycerol properties by measuring the speed of sound

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Abstract

The speed of sound in the liquid glycerol was calculated from the wave propagation time measurement in through transmission mode by using a designed acoustical cell. Measurements were carried out at atmospheric pressure and temperatures ranging from 298.47 K to 353.16 K. The proposed approach provided glycerol speed of sound values with experimental uncertainty of 1.9 m.s⁻¹. The data were compared with the values from literature resulting in relative deviations around the range of 0.5%. The data were also used to develop an empirical equation for the calculation of the speed of sound covering the considered temperature range, with standard deviation σ=2 m.s⁻¹.

KEYWORDS: Acoustic cell; Glycerol; Speed of sound; Empirical correlation

1. Introduction

Glycerol is mostly obtained from triglycerides, which are present in the plants and animal sources. The chemical processes as the hydrolysis and transesterification of the triglycerides give rise to glycerol and fatty acid alkyl esters (biodiesel). The glycerol from biodiesel industry (bio-glycerol) has been refined to an acceptable purity in dedicated refineries and then is sold at low prices as refined glycerol or refined to the grade United States Pharmacopeia which is suitable for food and pharmaceutical products. [1]

In recent years large quantities of crude glycerol were produced resulting in the decrease in price. This event has led to intensive research on its use according to appropriate technologies, as a renewable resource for energy and chemicals. Thus, new bio-glycerol routes have emerged, aimed at the production of glycerol derivatives to be used in fields as diverse as fuels, chemicals, pharmaceuticals, detergents, automotive and construction industries. Some important applications involve thermochemical conversions as combustion, gasification and pyrolysis. Gasification (e.g. Syngas production) and pyrolysis (e.g. bio-oil production) offer greater efficiency in energy production and less pollution [2]. Bio-glycerol is used as one of the most important component in biorefinery processes as is the case of the Glycell process where crude biodiesel glycerol is used as
the enhancer to efficiently decompose plant biomass into lignin, cellulose, and hemicellulose at low temperature and pressure [3]. The process allows to obtain biobased chemicals, biopolymers, and biofuels [4]. Important processes using bio-glycerol are related to glycerol fermentation to produce value-added bio-products, such as 1,3-propanediol, dihydroxyacetone, succinic acid, propionic acid, ethanol, butanol, hydrogen, citric acid, lactic acid, glycolic acid, biosurfactants, pigments and polyhydroxyalkanoates. [5]

As the glycerol is a raw material with increasing potential, the evaluation of its thermophysical properties has crucial importance in the classical, new industrial, and bio-based processes. The speed of sound is an important and very useful property for determining other thermodynamic properties indirectly as density and thermomechanical coefficients. [6]

Speed of sound data about glycerol are scarce in the literature and present some inconsistency.

In this work, the speed of sound in glycerol was measured at atmospheric pressure and temperatures from 298.43 K to 353.34 K. These measurements when compared with others considered as the most reliable from literature, frame and reinforce the dependency of speed of sound in extended range of temperatures.

2. Materials and methods

2.1 Materials

Glycerol was supplied by Fisher (CAS number 56–81-5) with stated mass fraction purity not less than 0.9995 and stated water content 4.59 x10^-4 in mass fraction. It was used without further purification

2.2 Speed of sound measurement

To measure the glycerol speed of sound, c, a stainless steel acoustical cell was used, which is represented in Figure 1 as (E7). The cell is composed by two modules of 60 mm in diameter. The liquid chamber has 6.28 cm³ of capacity. Two 5 MHz central frequency probes with 10 mm active diameter, are mounted on the top of steel modules. The complete instrumentation for the proposed goal is shown in Figure 1. Follows the description of the experimental and the procedure. The main equipment is identified by letter E, the measuring equipment by I, and valves by V. A Ruthe® 10 mL reusable glass syringe (E1) with a special locking tip (Luer lock), was used to fill up the cell chamber with the samples to be studied.

A thermostatic bath was used to heat the liquids and the temperature was maintained and controlled by using a Fisher Polystat 37 circulator (E6) with a stability 0.02 K. The temperature of samples was measured by ITS90 certified Isotech TTI-10 thermometer (I2), which was inserted in a deep hole drilled in the cell. The uncertainty of this standard thermometer was of u(T) = 0.01 K. The temperature inside the cell was maintained within 0.05 K.

For the acquisition of ultrasonic signals, the through-transmission methodology was used, where one probe acts as transmitter and the opposite one as receiver. In this approach, a wide band pulse is sent to the transmitter probe, using the pulser-receiver (E2).
Then, the generated acoustic wave propagates through the steel buffers and testing liquid, and reaches the receiver probe. This signal, corresponding to the direct path between the emitter and receiver is displayed on an oscilloscope (Tektronix TDS 2012B (100MHz) (E3), and then saved for further detailed analysis. In order to have an accurate and automatic measuring of the time of flight ($\Delta \tau$) in the liquid samples, it was developed a code in Matlab. That parameter, which is very important to extract the calibration equation for the speed of sound calculation, is obtained making the difference between the propagation time from emitter to receiver and the propagation time in the steel buffers. Taking into account all the possible sources of uncertainty, the combined standard uncertainty in the speed of sound was estimated to be $\sigma_c = 1.9 \text{ m.s}^{-1}$.

2.3 Calibration of the acoustic cell

The speed of sound, ignoring diffraction corrections, is obtained from the measured time of flight, $\Delta \tau$, and the known cell length ($L$), as:

$$c = \frac{L}{\Delta \tau}$$

(1)

The use of Eq. 1 requires the knowledge of the $L$ with great accuracy. Besides, some dimensional changes can occur with temperature. Thus, in order to avoid errors in the propagation path of the acoustic wave, a relative method was used. In this method the sound speeds of water, $c_{H2O}$ and glycerol, $c$, and the respective time of flight, $\Delta \tau$, are simultaneously compared. From Eq. 1, results,

$$c_{glyc} = c_{H2O} \frac{\Delta \tau_{H2O}}{\Delta \tau_{glyc}}$$

(2)

The wave propagation time in water ($\Delta \tau_{H2O}$) was obtained for the temperature range 299.08 K to 353.23 K, using the setup of Figure 1. The fitting of those data led to the empirical Eq. 3,

$$\Delta \tau_{H2O} = 40.7053 - 0.272709*(T/K) + 0.00071908*(T/K)^2 - 6.27683x10^{-7}*(T/K)^3$$

(3)

with determination coefficient $r^2 = 0.997$ and standard deviation $4.5 \times 10^{-3} \mu$s.

The corresponding values of speed of sound of water were taken from NIST [7] with
maximum uncertainties of 0.1 m.s\(^{-1}\) determined by the authors, by comparison with standard values from literature. The following equation was obtained by fitting:

\[
c_{H2O} = -5344.47 + 53.1108 \times (T/K) - 0.134243 \times (T/K)^2 + 0.000110912 \times (T/K)^3
\]  

(4)

with determination coefficient \(r^2 = 1.000\) and standard deviation 0.03 m.s\(^{-1}\). The maximum expected uncertainty for the speed of sound, \(\sigma_c\), can be predicted from the error propagation law applied to equation 2:

\[
\sigma_c = \sqrt{\left(\frac{\Delta t_{H2O}}{\Delta t_{Glyc}}\right)^2 \sigma_{c_{H2O}}^2 + \left(\frac{c_{H2O}}{\Delta t_{Glyc}}\right)^2 \sigma_{\Delta t_{H2O}}^2 + \left(\frac{c_{\Delta t_{H2O}}}{\Delta t_{Glyc}}\right)^2 \sigma_{\Delta t_{Glyc}}^2}
\]  

(5)

Taking the uncertainties in the speed of sound of water \(\sigma_{c_{H2O}} = 0.03\) m.s\(^{-1}\) and in the time of flight for water and glycerol as \(\sigma_{\Delta t_{H2O}} = \sigma_{\Delta t_{Glyc}} = 4.5 \times 10^{-3}\) µs, the combined uncertainty \(\sigma_c = \pm 1.9\) m.s\(^{-1}\) was obtained.

3. Results

The measured speed of sound as function of temperature, is presented in Table 1.

<table>
<thead>
<tr>
<th>T/K</th>
<th>(c / (\text{m.s}^{-1}))</th>
<th>T/K</th>
<th>(c / (\text{m.s}^{-1}))</th>
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<tr>
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<td>333.06</td>
<td>1826</td>
</tr>
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<td>303.25</td>
<td>1898</td>
<td>338.17</td>
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<tr>
<td>338.17</td>
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</tbody>
</table>

\(^{a,b}\) Two different samples of glycerol.

The fitting of data of table 1 to a quadratic function on temperature led to:

\[
c/(\text{m.s}^{-1})=1963.09 + 1.66486 \times (T/K) - 0.00620823 \times (T/K)^2
\]  

(6)

with determination coefficient \(r^2=0.998\) and standard deviation 2.0 m.s\(^{-1}\). The values of \(c\) listed in Table 1 and data from literature are plotted as function of temperature in Figure 2, for comparison. Considering that Eq. (6) represents data of this work, the relative deviations between calculated and literature data are plotted in Figure 3.
Figure 2. Speed of sound of glycerol, $c$, as a function of temperature, $T$.

From Figure 2 it can be concluded that data from Bhagavantam and Rao deviates significantly from those of this work, 2.3% in average. From Figure 3 it can be concluded that most of author’s data are in good agreement with those from this work in the range 280 K to 330 K with deviations around 0.5%.

Figure 3. Relative deviations between speed of sound of this work (eq 6) and values from literature, $c$.

4. Conclusions

Speed of sound measurements in glycerol were performed at atmospheric pressure at temperatures ranging from 298.43 K to 353.34 K, with experimental uncertainty of 1.9 m.s$^{-1}$. The measurements compared with values from literature showed relative deviations usually in the range of 0.5%. The data were used to develop an equation for the calculation of the speed of sound in glycerol in the range 298.47 K to 353.16 K with standard deviation, $\sigma=2$ m.s$^{-1}$. 
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References and footnotes