Speed of sound and density of ethanol-water mixture across the temperature range 10 to 50 degrees Celsius

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Abstract. Properties such as the speed of sound and density of ethanol-water mixtures are of concern in applications such as the calibration of ultrasound imaging machines, and the study of molecular interactions in binary solutions. The speed of sound and density in ethanol-water mixtures up to a concentration of 40% (w/w) were measured across the temperature range 10 to 50 °C using an ultrasound resonator and a densitometer, with accuracies of ±0.25 m/s and ±0.05 kg/m³, respectively. Measured data were interpolated and presented in forms of multi-polynomial functions of the concentration and the temperature. The functions may serve as a database for reference and also a source to derive parameters such as the temperature coefficient of the speed, the thermal expansion coefficient, and the isentropic compressibility of the mixture, which are commonly used in physiochemical and molecular acoustics studies.

1. Introduction
Ethanol-water mixtures can be used in ultrasound test objects as sound propagation media to assess medical ultrasound scanners. A mixture with a speed of sound of 1540 m/s is often used for testing the measurement tools provided by the imaging system [1]. Mixtures of other speed of sound, obtained by altering the ethanol concentration in the mixture, can be used in phantoms for assessing bladder volume. The speed of sound and the density in the mixture are also of interest in the study of molecular interactions [2]. It is therefore desirable to have a data source which gives the speed of sound and the density in the mixtures by simply specifying their concentration and temperature. Since the speed of sound has often been measured in-house, there are few numerically accessible data available in the literature [3-5]. Giacomini [3] measured the speed of sound in some ethanol-water mixtures with an uncertainty of about ±2 m/s; Martin and Spinks [4] measured the speed of sound in some mixtures with an uncertainty of about ±1.5 m/s. However, both the measurements were made at a few scattered ethanol concentrations and temperatures, which made the prediction of the speed within the concentration range and the temperature range less reliable. In addition, the data were presented in graphs instead of numerical values. Graph reading errors, which could be up to ±5–10 m/s and ±2–4 m/s in the two papers respectively, significantly reduce the usability of the data. Furthermore, there were no corresponding density data available from either set of authors.

In this work, we measured the speed of sound and density in ethanol-water mixtures at higher accuracies. The speed of sound and density were obtained in mixtures of concentrations of 0–40% (w/w) across the temperature range 10–50 °C. The results were presented as numerical expressions in
the form of multi-variant polynomial functions to provide a reference for not only the ultrasound quality assurance community but also those in physiochemical or molecular acoustics study.

2. Methods and materials

2.1. Density measurement
The densities of the mixtures were measured using an `Anton Paar DMA 4500M` densitometer (Anton Paar GmbH, Austria), based on the oscillating U-tube method [6]. A U-shaped borosilicate glass tube is filled with the measured sample and is then exited so that it vibrates at its characteristic frequency. This characteristic frequency is mass-sensitive and thus related to the density of the material in the tube. By determining the two characteristic frequencies when the tube is filled with the sample and with a standard material, the density of the sample \( \rho \) is obtained using the relation 
\[
\rho = \frac{f_2^2}{f_1^2} \left( K_A \times f_{\text{sample}} \times f_{\text{ref}} ^2 \times g_2 \right) - \left( K_B \times g_1 \right).
\]
Where \( f_{\text{sample}} \) and \( f_{\text{ref}} \) are the characteristic frequencies of the tube with the sample and with the standard, respectively; and \( K_A, K_B, g_1, \text{ and } g_2 \) are constants determined from the physical properties of the tube. During the measurement, the sample temperature was controlled to an accuracy of \( \pm 0.03 \, ^\circ C \), guaranteeing a density measurement accuracy of \( \pm 0.05 \, \text{kg/m}^3 \) [6].

2.2. Speed of sound measurement
The speed of sound was measured using an ultrasound resonator, the `ResoScan Research System` (IF Instruments GmbH, Germany). This instrument is a fixed-path ultrasound interferometer based on the method developed by Egges et al [7]. Two piston transducers are held parallel to one another to form an interferometer. Ultrasound standing waves are generated between the two transducers and the resonant frequency is identified. The speed of sound \( c \) is obtained by determining the resonance frequency \( f_n \) at which the sound path length \( l \) is equal to a whole number \( n \) of half-wavelengths \( \lambda/2 \), with the relation 
\[
c = 2f_n / n.
\]
The system had a sample cell with a volume of 170 µL and the sound path of 7 mm. The small sample volume made accurate temperature control possible, with a stability of \( 10^{-3} \, ^\circ C \) and an accuracy of 0.05 \(^\circ C\) when running at temperatures of 5–85 \(^\circ C\). Working in the frequency range 7.5–9.5 MHz and with techniques to minimise amplitude and phase ambiguities, the system gave the speed of sound with an accuracy of about \( \pm 0.25 \, \text{m/s} \) and a resolution of 0.001 m/s [8].

2.3. Materials and measurement procedures
Ethanol (99.1% v/v) was obtained from Rathburn Chemicals (Mfg) Ltd, Walkerburn, UK. Deionised distilled water was made in-house. The ethanol-water mixtures were made by mixing a certain amount of the ethanol pre-determined by weight with the water without further purification. The mixtures were left to stand still for about 1–2 hours before samples were taken for the measurements.

To determine the ethanol concentration of a mixture, first the density was measured and its value at 20 \(^\circ C\) was taken. Then the value was used with the ethanol tables of the International Union of Pure and Applied Chemistry (IUPAC) provided with the densitometer, to give the concentration as both a weight percentage (% w/w) and a volume percentage (% v/v). With the density measured within \( \pm 0.05 \, \text{kg/m}^3 \), the concentration was obtained with an accuracy of about \( \pm 0.025% \) (w/w) or \( \pm 0.031% \) (v/v).

Seventeen mixtures with ethanol concentrations ranging from 3–40 % (w/w) were prepared, each of them with a volume of more than 500 ml. The density was measured in the mixture samples across the temperature range 10–50 \(^\circ C\) with a step size of 2 \(^\circ C\). The speed of sound was measured in the mixture samples across the same temperature range but with a temperature changing rate of 0.3 K/minute, with a measurement rate of 60 measurements per minute. Each sample was measured twice in a temperature rising and falling cycle. The averaged value at the same temperature in the cycle was taken for the speed value. The total measurement time for each sample was about 4–5 hrs.
3. Results and discussions

3.1. Density results

The density of the in-house water was measured to verify its purity. At 20 °C, the measured value was 998.21 kg/m³, which is in agreement with the value 998.2063 kg/m³ from the literature [5]. This ensured the usability of the water.

Densities of 17 mixtures, together with those of water and ethanol, were obtained. The concentrations, obtained using the IUPAC ethanol table with a density value at 20 °C, were obtained as both a weight percentage \( \xi \) (in % w/w) and a volume percentage \( \varphi \) (in % v/v) at 20°C. The two concentrations were related via the expression

\[
\varphi = 0.016 + 1.254 \xi - 9.963 \times 10^{-4} \xi^2 - 1.836 \times 10^{-5} \xi^3, \quad 0 < \xi < 40
\] (1)

This expression was obtained using the Mathcad® software package (Parametric Technology Corporation, MA, USA) with a least-squares polynomial fit algorithm [9]. An error estimate \( \varepsilon \), defined as

\[
\varepsilon = \left( \sum_i \left( (y_i - Y_i)^2 / y_i \right) / m \right)^{0.5}
\]

for assessing the goodness of fit (eliminating any singular points), was found to be of the order of 10⁻⁴. In the definition, \( y_i \) and \( Y_i \) are the \( i \)th measured and fitted data, respectively, and \( m \) is the total number of the measured data.

In order to present the density values numerically, a least-squares multi-variant polynomial fit algorithm in Mathcad® [9] was used to obtain the density as a function of the concentration \( \xi \) (in % w/w) and the temperature \( T \) (in °C). With a polynomial of order 7, the density was given in kg/m³ in the form

\[
\rho(\xi, T) = \sum_{i=1}^{36} A_i \xi^M T^N, \quad 0 \leq \xi < 40, \quad 0 \leq T \leq 50
\] (2)

where \( A, M \) and \( N \) were matrices of 36 components, whose values are shown in Table 1.

The polynomial of order 7 was used for two reasons: 1) the order should not be too large so that few polynomial terms were involved; 2) the order should be large enough so that reasonable accuracy of the interpolation prediction could be maintained. With an order of 7, the error estimate for Eq. (2) was about 10⁻⁶.

With the same polynomial order, density values \( \rho_p(T) \) (in kg/m³) for the ‘pure’ ethanol (98.49% w/w or 99.1% v/v) were given in the form:

\[
\rho_p(T) = 810.410 - 0.6909797T - 1.94981 \times 10^{-2} T^2 + 1.28718 \times 10^{-3} T^3 - 4.95359 \times 10^{-5} T^4 + 1.08911 \times 10^{-6} T^5 - 1.27659 \times 10^{-6} T^6 + 6.17318 \times 10^{-11} T^7, \quad 10 \leq T \leq 50
\] (3)

The error estimate for Eq. (3) was about 10⁻⁶.

3.2. Speed of sound results

The speed of sound was obtained at frequencies between 7.5 MHz and 8.5 MHz. Within this frequency range, no speed dispersion greater than 0.05 m/s was found for mixture samples.

The same polynomial algorithm with a polynomial of order 10 was applied to the measured data to get the speed of sound in the form:
\[ c(\xi, T) = \sum_{i=1}^{66} D_i \xi_i^K T^L_i, \quad 0 \leq \xi \leq 25, \quad 0 \leq T \leq 50 \] (4)

where \( D, K \) and \( L \) were matrices of 66 components, whose values are shown in Table 1.

**Table 1.** Matrix components in the polynomial expressions of the density and the speed of sound.

| i  | Ai     | Mi | Ni | Di          | Ki | Li | i  | Di          | Ki | Li   |
|----|--------|----|----|-------------|----|----|----|-------------|----|------|
| 1  | -1.31979E-10 | 1  | 6  | 2.293523E-13 | 1  | 9  | 37 | 2.581214E+00 | 0  | 2    |
| 2  | 9.26559E-11  | 0  | 7  | -3.334069E-14 | 0  | 10 | 38 | -9.778700E-02 | 1  | 2    |
| 3  | -1.84296E-08 | 0  | 6  | 4.347779E-12 | 0  | 9  | 39 | -3.409837E-03 | 2  | 2    |
| 4  | 1.48789E-06  | 0  | 5  | 2.748470E-10 | 0  | 8  | 40 | 9.554803E-05  | 3  | 2    |
| 5  | 2.68566E-08  | 1  | 5  | -6.740920E-11| 1  | 8  | 41 | -2.029789E-06 | 4  | 2    |
| 6  | -1.17238E-10 | 2  | 5  | 4.872988E-14 | 2  | 8  | 42 | 7.303260E-08  | 5  | 2    |
| 7  | -6.27703E-05 | 0  | 4  | -9.379410E-08| 0  | 7  | 43 | -2.678939E-09 | 6  | 2    |
| 8  | -2.24365E-06 | 1  | 4  | 8.441089E-09 | 1  | 7  | 44 | 5.681490E-11 | 7  | 2    |
| 9  | 2.47408E-08  | 2  | 4  | -7.191991E-12| 2  | 7  | 45 | -4.742113E-13 | 8  | 2    |
| 10 | -1.34332E-10 | 3  | 4  | -3.459921E-14| 3  | 7  | 46 | -1.154564E-01 | 0  | 1    |
| 11 | 1.51236E-03  | 0  | 3  | 8.520253E-06 | 0  | 6  | 47 | 2.115519E-01  | 1  | 1    |
| 12 | 9.82635E-05  | 1  | 3  | -5.876577E-07| 1  | 6  | 48 | 5.354679E-02  | 2  | 1    |
| 13 | -2.06834E-06 | 2  | 3  | -2.717664E-11| 2  | 6  | 49 | -8.378834E-03 | 3  | 1    |
| 14 | 2.53304E-08  | 3  | 3  | 1.566856E-11 | 3  | 6  | 50 | 1.154267E-03  | 4  | 1    |
| 15 | -1.19569E-10 | 4  | 3  | -7.961328E-14| 4  | 6  | 51 | -9.631472E-05 | 5  | 1    |
| 16 | -2.65277E-02 | 0  | 2  | 2.175723E-04 | 0  | 5  | 52 | 4.720320E-06  | 6  | 1    |
| 17 | -2.38970E-03 | 1  | 2  | 2.487626E-05 | 1  | 5  | 53 | -1.331721E-07 | 7  | 1    |
| 18 | 8.12064E-05  | 2  | 2  | 6.317368E-08 | 2  | 5  | 54 | 2.000458E-09  | 8  | 1    |
| 19 | -1.09917E-06 | 3  | 2  | -2.116633E-09| 3  | 5  | 55 | -1.238626E-11 | 9  | 1    |
| 20 | -3.79088E-10 | 4  | 2  | 1.542227E-11 | 4  | 5  | 56 | 1.446424E+03  | 0  | 0    |
| 21 | 7.42769E-11  | 5  | 2  | -2.889305E-14| 5  | 5  | 57 | 1.142117E+01  | 1  | 0    |
| 22 | 1.72377E-01  | 0  | 1  | 1.246830E-02 | 0  | 4  | 58 | -8.523948E-01 | 2  | 0    |
| 23 | 3.03939E-02  | 1  | 1  | -6.572525E-04| 1  | 4  | 59 | 3.394837E-01  | 3  | 0    |
| 24 | -1.91310E-03 | 2  | 1  | -4.957552E-06| 2  | 4  | 60 | -6.665556E-02 | 4  | 0    |
| 25 | -2.95143E-06 | 3  | 1  | 1.370765E-07 | 3  | 4  | 61 | 7.478822E-03  | 5  | 0    |
| 26 | 1.02853E-06  | 4  | 1  | -1.363176E-09| 4  | 4  | 62 | -5.137953E-04 | 6  | 0    |
| 27 | -6.76030E-09 | 5  | 1  | 8.968693E-12 | 5  | 4  | 63 | 2.187272E-05  | 7  | 0    |
| 28 | -7.56401E-11 | 6  | 1  | -4.644391E-14| 6  | 4  | 64 | -5.617519E-07 | 8  | 0    |
| 29 | 9.96163E+02  | 0  | 3  | -2.323159E-01| 0  | 3  | 65 | 7.949837E-09  | 9  | 0    |
| 30 | -2.06524E+00 | 1  | 0  | 1.065812E-02 | 1  | 3  | 66 | -4.745228E-11 | 10 | 0    |
| 31 | 4.69556E-02  | 2  | 0  | 1.790475E-04 | 2  | 3  | 32 | 6.00674E-04  | 3  | 3    |
| 33 | -6.78157E-05 | 4  | 0  | 5.512563E-08 | 4  | 3  | 34 | 1.18896E-06  | 5  | 3    |
| 35 | -1.13524E-08 | 6  | 0  | -6.812776E-12| 6  | 3  | 36 | 9.52109E-11  | 7  | 3    |
In Eq. (4) the valid concentration range was narrowed down to 0–25% (w/w) to avoid larger errors of the interpolation prediction, which was induced by the fact that there were only three measured mixtures in the range of \(25 < \xi < 40\) and also by the fact that the polynomial prediction, by its nature, fluctuates when raw data spacing becomes large. In the Eq. (4), the error estimate for the speed data fitting was of the order of \(10^{-3}\). The maximum residual between the measured speed and the predicted value from Eq. (4), defined as \(\chi = \max|c - c(\xi, T)|\), was 1.51 m/s.

Values from Eq. (4) at \(\xi = 0\) were compared with those given by Grosso (cited as Table 1 in the literature [4]) who measured the speed of sound in water at various temperatures with an accuracy of \(10^{-3}\%\). The standard deviation of the difference between Grosso’s values and those from Eq. (4) was 0.097 m/s. This shows that the expression could give reasonably accurate predictions, especially at or near to the measured data points.

Similar to the density, the speed of sound for the ‘pure’ ethanol was given as

\[
c_p(T) = 1219.90 - 0.023127T - 0.418307T^2 + 0.026607T^3 - 9.91594 \times 10^{-4} T^4 + 2.05985 \times 10^{-5} T^5 - 2.34839 \times 10^{-7} T^6 + 1.10971 \times 10^{-9} T^7, \quad 10 \leq T \leq 50
\]

(5)

The error estimate for the expression was of the order of \(10^{-5}\).

3.3. Discussions
The advantage of Eqs. (1)-(5) is the convenience for accessing numerical values of the speed of sound and the density of ethanol-water mixtures. For example, given a speed of sound of 1540 m/s and a tolerance of ±2 m/s, one can easily determine that, working in the temperature range of 19–21 °C, the mixture which has the specified speed of sound must lie in a diamond-shaped area in the speed against concentration and iso-temperature curve surrounded by four points (weight concentration %, temperature °C): (6.8, 21), (7.33, 21), (7.77, 19) and (7.28, 19). Expressed in the volume concentration (% v/v) at 20 °C, the four points are (8.49, 21), (9.15, 21), (9.69, 19) and (9.09, 19).

Martin and Spinks [4] pointed out that, at 20 °C a mixture of 9.5 ± 0.25 % (v/v) has a speed of sound of 1540 m/s. Using Eq. (4), the mixture of the concentration 9.5 % (v/v) at 20 °C is of the speed of sound of 1542.56 m/s. Since Martin and Spinks did not specify the temperature at which the mixture concentration was obtained, the difference between their results and our results here could be partially due to the uncertainty of the volume concentration, which varies as the temperature changes.

Another advantage is that numerical values for various derivatives of the speed of sound, and the density, can be easily derived from the equations. Those derivatives, such as the temperature coefficient of the speed of sound, the thermal expansion of the mixture, the isentropic compressibility, the excess volume of the mixtures, etc, can be important parameters in the physiochemical study or the molecular acoustics study of the mixtures [2, 10].

4. Conclusions
The speed of sound and density of ethanol-water mixtures with concentrations of up to 40% (w/w) were measured across the temperature range 10–50 °C. The measurement accuracies were of ±0.25 m/s and ±0.05 kg/m³, respectively. The values were expressed as numerical equations, with prediction uncertainties better than about \(10^{-3}\) and \(10^{-6}\), respectively.
5. References

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