

## Measurement of the Temperature and Concentration Dependent Sound Velocity in Ethanol-Water Liquid Mixtures

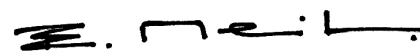
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**Abstract:** The sound velocity  $v_s$  of pure water and pure ethanol and of their mixtures have been measured with an ultrasonic echometer. In general, liquids of a given composition showed strong temperature dependence in the observed temperature range 20–50 °C. The sound velocity of pure water and water-rich mixtures was found to increase with temperature, whereas in pure ethanol and ethanol-rich mixtures the sound velocity shows the opposite effect. In pure water,  $v_s(T)$  increases nonlinearly with an extrapolated maximum at around 68 °C. In pure ethanol and in the same temperature range,  $v_s(T)$  decreases linearly. 22.2 °C and 27.6 °C isotherms of  $v_s$  of ethanol-water mixtures over the whole composition range both show a maximum in the water-rich region around  $x_{\text{EtOH}} \approx 0.15$ . From these isotherms, the temperature coefficient of the sound velocity at 25 °C could be determined as a function of composition. This allowed to identify a mixture with the property of a vanishing temperature coefficient. This particular mixture is characterized by its mole fraction  $x_{\text{EtOH}} = 0.0635 \pm 0.0011$  and constant sound velocity of  $v_s = 1594.9 \pm 1.2 \text{ m s}^{-1}$ .

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## Introduction

Sound velocity measurements can be used to determine various thermodynamic properties of gases, liquids and solids. Since, e.g., the sound velocity  $v_s$  is related to the density  $\rho$  and to the adiabatic (isentropic) compressibility  $\kappa_S$  by

$$v_s^2 = \frac{1}{\rho \kappa_S} \quad \text{with} \quad \kappa_S = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_S, \quad (1)$$

compressibility data are easily accessible through  $v_s$  (and density) measurements, contrary to direct pressure ( $p$ ) and volume ( $V$ ) measurements at constant entropy  $S$  (see [1]).

Liquid alcohol-water mixtures show unusual properties especially in the water-rich region. These are generally explained by molecular association that leads to cluster formation. To mention just a few, the concentration dependencies of the molar heat capacity, the partial molar volumes, the heat of mixing and the sound velocity all exhibit strong deviations from the behaviour of ideal systems [2]. The sound velocity in pure water and in pure ethanol strongly—and oppositely—depends on temperature, and in mixtures, the sound velocity additionally depends on the composition [3–7].

It is the aim of this work to reinvestigate these already known dependencies by means of a sound velocimeter that measures the travel time of echo signals in the liquid. As a result of our investigation, we suggest a specific ethanol-water mixture as a test liquid with a temperature-independent sound velocity.

The large concentration dependence of  $v_s$  in mixtures makes sound velocimetry also a fast and simple analytical tool, since modern ultrasound velocimeters are easily handled and applied to many types of liquids.

## Experimental

**Chemicals:** Water,  $M_{\text{H}_2\text{O}} = 18.02 \text{ g mol}^{-1}$ , was used in ultrapure quality from a TKA GenPure UV-TOC water purification system, with  $0.055 \text{ }\mu\text{S cm}^{-1}$  specific conductance at dispenser. Ethanol,  $M_{\text{EtOH}} = 46.07 \text{ g mol}^{-1}$ , from FLUKA, puriss. p.a.,  $\geq 99.5\%$ , was used without further purification.

**Solution preparation:** Each mixture was prepared with the aid of a BRAUN Omnifix 50 mL polypropylene syringe, equipped with a 100 mm stainless steel needle. The syringe was weighed on an analytical balance (METTLER-TOLEDO XA 2014 DR, 0.1 mg) first in empty state and subsequently after loading with appropriate amounts of pure ethanol (mass  $m_{\text{EtOH}}$ ) and then pure water (mass  $m_{\text{H}_2\text{O}}$ ) up to a total volume of ca. 30 mL. The long needle efficiently prevented loss of liquid due to evaporation. The liquid was mixed in the syringe to give samples with reliable weight (mass) fractions  $w_{\text{EtOH}}$  or mole fractions  $x_{\text{EtOH}}$  of ethanol,

$$w_{\text{EtOH}} = \frac{m_{\text{EtOH}}}{m_{\text{EtOH}} + m_{\text{H}_2\text{O}}}, \quad x_{\text{EtOH}} = \frac{m_{\text{EtOH}}/M_{\text{EtOH}}}{m_{\text{EtOH}}/M_{\text{EtOH}} + m_{\text{H}_2\text{O}}/M_{\text{H}_2\text{O}}} \quad (2)$$

The liquid mixture was transferred to a home-built 30 mL glass sample tube (20 mm diameter) equipped with a thermostating water jacket (see Fig. 1). A LAUDA B/M3 thermostat was used to maintain the sample with circulating water at preset temperatures between 20–50 °C.

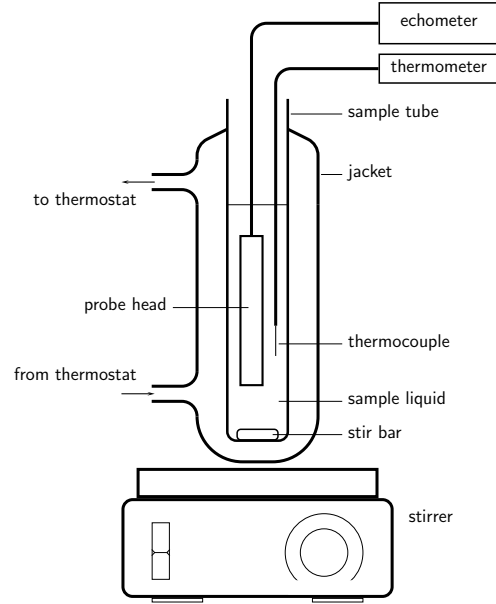


Figure 1: Experimental setup to measure the sound velocity of liquid thermostated samples. Details see text.

**Measurements:** The sample temperature was measured by means of a GREISINGER GMH 3210 digital thermometer with  $0.1\text{ }^\circ\text{C}$  resolution, coupled to a GTF 300 NiCr thermocouple wire. Accuracy of the thermometer was checked with ice-water slurry in a Dewar vessel and showed only neglecting deviation of  $-0.1\text{ }^\circ\text{C}$  from  $0\text{ }^\circ\text{C}$ . After equilibration the thermostat-controlled samples were stable to within  $\pm 0.1\text{ }^\circ\text{C}$ .

Sound velocities of the liquids were measured with a KARL DEUTSCH Echometer 1076 K, operating at  $4\text{ MHz}$  ultrasonic frequency, with the stainless steel probe immersed in the thermostatted sample. The instrument actually measures, with a piezo microphone, the travel time of echoes of short ultrasound burst signals in the  $2\text{ cm}$  resonator of the probe head. Readings were generally constant to  $\pm 0.1\text{ m s}^{-1}$ . A reference value of  $1496.7\text{ m s}^{-1}$  for the sound velocity in pure water at  $25\text{ }^\circ\text{C}$  was used to determine a correction factor of  $0.9923$  to our velocity measurements [8]. Between measurements of different samples the sample tube, the echometer probe and the thermocouple were dried with tissue paper.

The temperature dependencies of the sound velocity in pure water and ethanol were measured in steps of  $2\text{--}3\text{ }^\circ\text{C}$ , starting at  $20\text{ }^\circ\text{C}$  up to a maximum temperature of ca.  $50\text{ }^\circ\text{C}$ , the upper limit given by the maximum operation temperature for the echometer probe head. Equilibration at these steps typically took ca.  $5\text{ min}$ .

The temperature coefficients ( $\Delta v_s/\Delta T$ ) of mixtures were determined with the aid of two separate identical thermostats, one running at  $\theta_1 = 22.2\text{ }^\circ\text{C}$  while the other was set to  $\theta_2 = 27.6\text{ }^\circ\text{C}$ . By simply opening and closing valves to the sample jacket the temperature of the mixtures could be cycled between  $\theta_1$  and  $\theta_2$ , yielding the sound velocities at these temperatures. Eq. (3) can be regarded as a good approximation to the temperature coefficient at  $25\text{ }^\circ\text{C}$  (the mean temperature) even of liquids with nonlinear  $v_s(T)$  behaviour (such as pure water).

$$\frac{v_s(\theta_2) - v_s(\theta_1)}{\theta_2 - \theta_1} = \left( \frac{\Delta v_s}{\Delta T} \right)_{25\text{ }^\circ\text{C}} \quad (3)$$

Temperatures  $\theta_1$  and  $\theta_2$  were selected due to satisfactory measurement precision of both temperature and sound velocity.

The R software environment [9] (version 3.1.2) was used for data processing, model parameter estimation and presentation.

## Results and Discussion

As has been reported in literature [3, 4], the sound velocity in the pure liquids water and ethanol both strongly depend on temperature. Our results, presented in Fig. 2, agree with their findings, showing an increase of  $v_s$  with temperature in case of water but a decrease in the case of ethanol. The origin of this opposed behaviour is that the compressibility of water decreases with rise of temperature, i.e.  $\partial\kappa_S/\partial T < 0$ , whereas for alcohols  $\partial\kappa_S/\partial T > 0$ .

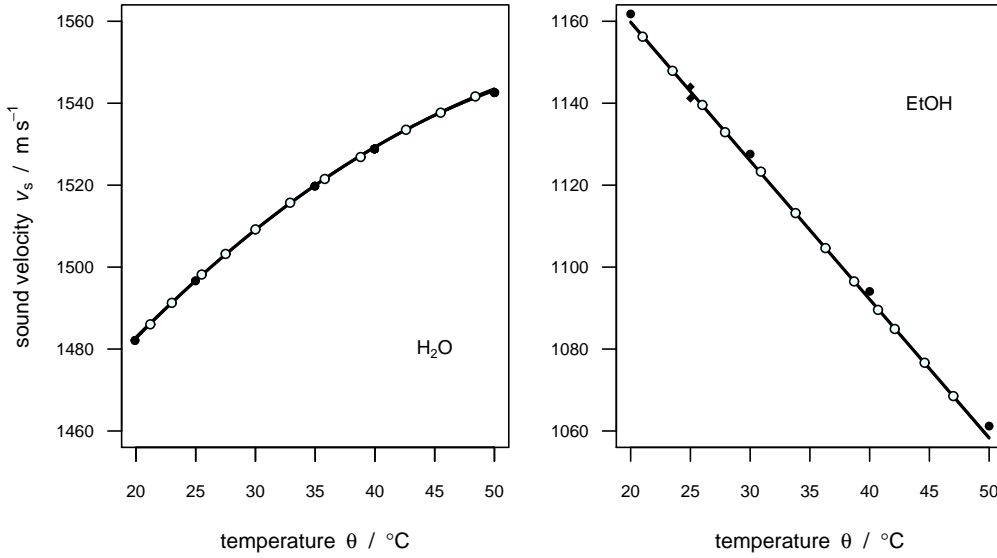


Figure 2: Sound velocity  $v_s$  in pure water (left panel) and in pure ethanol (right panel) as a function of temperature  $\theta$ . Water shows a nonlinear increase in the observed temperature range, whereas ethanol exhibits a stronger linear decrease, as described by Eqns. (4) and (5), respectively. Identical span of ordinate scales was chosen for easier comparison. Experimental data (o) are close to literature values ( $\bullet$ ,  $\blacklozenge$ ) from different sources, see Table 1.

Quadratic regression to our experimental data of water between 20 °C to 50 °C gives

$$v_s(\text{H}_2\text{O}) = a_0 + a_1\theta + a_2\theta^2 \quad \begin{cases} a_0 = 1411.6 \pm 2.1 \text{ m s}^{-1} \\ a_1 = 4.18 \pm 0.13 \text{ m s}^{-1} \text{ K}^{-1} \\ a_2 = -(30.8 \pm 1.9) \cdot 10^{-3} \text{ m s}^{-1} \text{ K}^{-2} \end{cases} \quad (4)$$

Our ethanol data follow the linear equation

$$v_s(\text{EtOH}) = b_0 + b_1\theta \quad \begin{cases} b_0 = 1227.4 \pm 0.5 \text{ m s}^{-1} \\ b_1 = -3.382 \pm 0.013 \text{ m s}^{-1} \text{ K}^{-1} \end{cases} \quad (5)$$

Uncertainties of the parameters in equations (4) and (5) are given as 95% confidence intervals. Calculated sound velocities for both liquids at selected temperatures are listed in Table 1. Comparison with reported data from different sources [3–6] shows excellent agreement.

Table 1: Sound velocity  $v_s$  of pure water and ethanol between 20–50 °C. Values from this work are calculated with Eqns. (4) and (5), respectively, with estimated uncertainties better than 1 m s<sup>-1</sup>.

$\theta / ^\circ\text{C}$	water		ethanol	
	$v_s / \text{m s}^{-1}$ this work	$v_s / \text{m s}^{-1}$ Lit.	$v_s / \text{m s}^{-1}$ this work	$v_s / \text{m s}^{-1}$ Lit.
20	1482.8	1482.1 [3]	1159.8	1161.78 [4]
25	1496.7	1496.2 [3]	1142.9	1144 [5], 1141.20 [6]
30	1509.1	1509.1 [3]	1126.0	1127.58 [4]
35	1520.0	1519.8 [3]	1109.0	
40	1529.3	1528.8 [3]	1092.1	1094.07 [4]
45	1537.1		1075.2	
50	1543.3	1542.6 [3]	1058.3	1061.20 [4]

The temperature dependence of the sound velocity in pure water shows a decreasing slope at increasing temperatures. One can therefore expect that  $v_s$  achieves a maximum at some specific temperature (which lies outside the temperature range investigated in this work). Using the parabolic approximation given in Eq. (4) this maximum can be located at ca.  $\theta = 68^\circ\text{C}$  and  $v_{s,\text{max}} = 1553 \text{ m s}^{-1}$  (with estimated uncertainties of ca.  $\pm 2^\circ\text{C}$  and  $\pm 2 \text{ m s}^{-1}$ , respectively). This extrapolation agrees well with a curve of  $v_s$  vs.  $\theta$  presented in [10]. The occurrence of a maximum in the sound velocity curve results from the combination of a decreasing density curve and a compressibility curve that goes through a minimum, see Eq. (1).

The opposite temperature dependence of the sound velocities in pure water and ethanol, shown above, and the reported strong dependence of  $v_s$  in mixtures of these solvents, motivated us to find a specific solution that shows a cancelled temperature effect. Fig. 3 shows the sound velocities of some ethanol-water mixtures measured at 22.2 °C and 27.6 °C, respectively. We could verify, starting with pure water, an increase of  $v_s$  with  $x_{\text{EtOH}}$ , followed by a steady decrease, with a maximum of  $v_s$  around  $x_{\text{EtOH}} \approx 0.15$ , as previously described by [7]. This effect is explained with the formation of clusters of ethanol and water in the solution, leading to a compressibility minimum. Inspection of Fig. 3 reveals that in liquids with low ethanol concentration the sound propagates faster with increasing temperature, whereas in liquids with high ethanol concentration the situation is reversed. Around  $x_{\text{EtOH}} \approx 0.06$  no temperature effect occurs to  $v_s$ . Note that location of the  $v_s$  maximum depends on the ethanol concentration, as can be seen by the "low temperature" and "high temperature" lines in Fig. 3. Both isotherms cross at a mixture composition with vanishing temperature effect to the sound speed, at approximately 17 percent by weight of ethanol, a value that has been determined by Giacomini [7] early in 1947.

A plot of the temperature coefficient ( $\Delta v_s / \Delta T$ ) of the sound velocity around 25 °C, determined as described in the Experiment section with Eq. (3), is shown in Fig. 4 as a function of the composition of the liquid. Generally, a decrease of the temperature coefficient is observed when going from pure water to pure ethanol. However, a strong decrease appears at low ethanol concentration ( $x_{\text{EtOH}} < 0.15$ ), followed by a much weaker decrease at moderate and high ethanol concentration. As expected, a zero temperature coefficient can be found at a specific ethanol-water composition. In the low ethanol concentration region, our experimental temperature coefficients could be well fitted by a 2nd degree polynomial, see Fig. 4. This function crosses ( $\Delta v_s / \Delta T$ ) = 0 at  $x_{\text{EtOH}} = 0.0635 \pm 0.0011$ , or  $w_{\text{EtOH}} = 0.148 \pm 0.003$ , respectively. A liquid

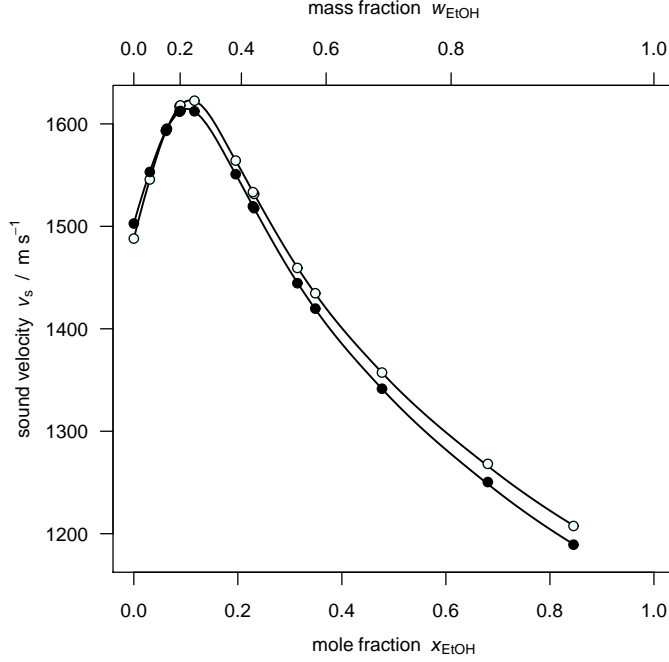


Figure 3: Sound velocity  $v_s$  of ethanol-water mixtures at  $22.2^\circ\text{C}$  ( $\circ$ ) and at  $27.6^\circ\text{C}$  ( $\bullet$ ). Bottom scale: mole fraction of ethanol,  $x_{\text{EtOH}}$ ; top scale: weight fraction of ethanol,  $w_{\text{EtOH}}$ . Both isotherms show a pronounced concentration dependence with slightly different maximum velocities. Note the reversed temperature effect at high and low concentration and the crossing of the isotherms.

with this composition does not exhibit any temperature dependence of its sound velocity  $v_s = 1594.9 \pm 1.2 \text{ m s}^{-1}$ , at least around  $25^\circ\text{C}$ . Uncertainties have been determined using the 95% confidence curves of the polynomial fit, as calculated with the regression function in the R software, details see Appendix. With  $14.8 \pm 0.3$  weight percent of ethanol our results confirm the previous value (17%) of Giacomini [7]. We suggest that this particular mixture can be used as a standard test substance for sound velocity measurements where constant temperature cannot easily be maintained. Whether the sound velocity of this mixture does not change also

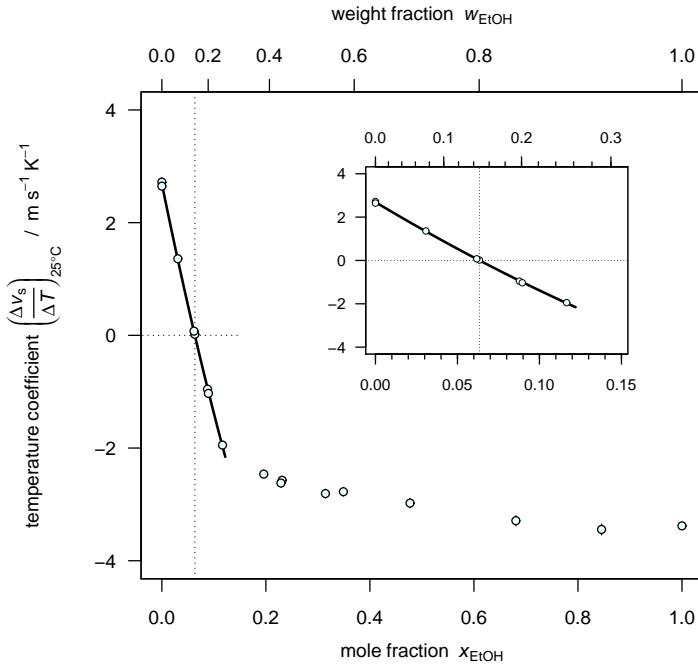


Figure 4: Temperature coefficient  $\Delta v_s / \Delta T$  at  $25^\circ\text{C}$  of the sound velocity in ethanol-water mixtures. Bottom scale: mole fraction of ethanol,  $x_{\text{EtOH}}$ ; top scale: weight fraction of ethanol,  $w_{\text{EtOH}}$ . Small error bars may be hidden by the circle symbols. A large change of the temperature coefficient occurs at low ethanol concentration (see enlarged region in the smaller figure). The bold line is a quadratic curve fit to the data at  $x_{\text{EtOH}} < 0.15$ . The temperature coefficient is zero in a mixture with  $x_{\text{EtOH}} = 0.0635 \pm 0.0011$  (or  $w_{\text{EtOH}} = 0.148 \pm 0.003$ ), indicated by dotted lines.

at some elevated temperature, has not been investigated in our work and could not be verified with literature data.

Our method to determine the emperature coefficient of the sound velocity of liquids proved to be successfull with high accuracy and precision and could be applied to other alcohol-water mixtures as well.

## References

- [1] E. Meister, *Grundpraktikum Physikalische Chemie. Theorie und Experimente*, 2nd edition, vdf Hochschulverlag AG an der ETH Zürich, Zurich, 2012.
- [2] F. Franks, D.J.G. Ives, The Structural Properties of Alcohol-Water Mixtures, *Quart. Rev. Chem. Soc.* **20** (1966) 1.
- [3] V.A. del Grosso, C.W. Mader, Speed of Sound in Pure Water, *J. Acoust. Soc. Am.* **52** (1972) 1442.
- [4] W. Wilson, D. Bradley, Speed of Sound in Four Primary Alcohols as a Function of Temperature and Pressure, *J. Acoust. Soc. Am.* **36** (1964) 333.
- [5] S.G. Bruun, P. Graae Sørensen, Ultrasonic Properties of Ethanol-Water Mixtures, *Acta Chem. Scand.* **A 28** (1974) 1047.
- [6] O. Kiyohara, G.C. Benson, Thermodynamics of Aqueous Mixtures of Nonelectrolytes. III. Compressibilities an Isochoric Heat Capacities of Water–n-Alcohol Mixtures at 25 °C, *J. Solution Chem.* **10** (1981) 281.
- [7] A. Giacomini, Ultrasonic Velocity in Ethanol-Water Mixtures, *J. Acoust. Soc. Am.* **19** (1947) 701.
- [8] W.M. Haynes, ed., *CRC Handbook of Chemistry and Physics*, 95th Edition (Internet Version 2015), CRC Press/Taylor and Francis, Boca Raton, FL.
- [9] R Core Team (2014), R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. <http://www.R-project.org/>.
- [10] [http://www1.lsbu.ac.uk/water/density\\_anomalies.html#sound](http://www1.lsbu.ac.uk/water/density_anomalies.html#sound), accessed Jan 5, 2015.

## Appendix

A1 – Lab journal copies, dated December 12 and 18, 2014.

A2 – Copies of references [2–7, 10].

## Acknowledgment

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