Thermodynamic speed of sound data for liquid and supercritical alcohols

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ABSTRACT: Because of their caloric and thermal nature, speed of sound data are vital for the development of fundamental Helmholtz energy equations of state for fluids. The present work reports such data for methanol, 1-propanol, 2-propanol and 1-butanol along seven isotherms in the temperature range from 220 K to 500 K and a pressure of up to 125 MPa. The overall expanded uncertainty varies between 0.07% and 0.11% with a confidence level of 95%. The employed experiment is based on a double path length pulse-echo method with a single piezoelectric quartz crystal of 8 MHz, which is placed between two reflectors at different pathlengths. Measured speed of sound data for the four alcohols are fitted with double polynomial equations and compared with literature sources.

1. Introduction

Although it plays an important role in the transport of pressure oscillations through matter, the speed of sound is a thermodynamic equilibrium property. This can directly be seen from its definition

$$w = \sqrt{(\partial p/\partial \rho)_s}, \tag{1}$$

where w is the speed of sound, p the pressure, ρ the density and s the entropy. It thus relates pressure to density variations under isentropic conditions, which are given for reversible processes in the absence of heat transfer. In case of typical sound emission scenarios, where amplitude and frequency are not excessive,[1] data on wave propagation timing indeed adhere to definition (1).

Because of the isentropic condition of the partial derivative in its definition (1), the speed of sound is not a purely thermal property. Instead, it contains information on the caloric behavior of matter. A less common expression for the speed of sound can be given in terms of the Helmholtz energy[2,3]

$$w^2/T = 1 + 2A_{01}^r + A_{02}^r - \frac{(1+A_{01}^r-A_{11}^r)^2}{A_{20}^0+A_{20}^r}. \tag{2}$$

Therein, T is the temperature and A_{mn} represent a normalized form of partial derivatives of the Helmholtz energy with respect to inverse temperature and density.[3] Subscript m stands for the order of the inverse temperature derivative and n for the order of the density derivative. In case of an ideal gas, the residual Helmholtz energy (superscript r) vanishes, while the ideal contribution (superscript 0) remains. Consequently, the well-known equation for the ideal gas emerges[4]

$$w^0 = \sqrt{\kappa RT}, \tag{3}$$

where R stands for the gas constant and κ is the heat capacity ratio. From equation (3), the caloric nature of the speed of sound becomes evident.

In general, measuring thermodynamic properties is a tedious and time-consuming undertaking, especially at elevated temperatures and pressures. However, speed of sound measurements can be accomplished comparably rapidly and yield data with a high accuracy. E.g., in the present work, about four weeks were required to measure one fluid in the considered temperature and pressure ranges.

Due to their caloric and thermal nature, temperature and pressure dependent speed of sound data can be integrated to yield both density and isobaric heat capacity. Properties calculated along that route may often be more reliable than direct measurements.[5]

Speed of sound data have also been used extensively as a basis for the development and parameterization of fundamental Helmholtz energy equations of state for fluids.[6,7] With these models, all time-independent thermodynamic properties can be calculated efficiently, i.e. without integration.

The aim of this work was to provide accurate speed of sound data for a group of primary alcohols, which are commonly used in numerous applications and industrial processes, e.g. as fuels, solvents, inhibitors, heat transfer agents or paint additives.[8–12] Consequently, precise thermodynamic data are needed for these alcohols over a wide span of temperature and pressure to develop high-quality Helmholtz energy equations of state.[7,13,14] Moreover, such data are important to validate speed of sound calculations by means of thermodynamic models.[15–18]

In this work, the pulse-echo technique was implemented to measure speed of sound of methanol, 1-propanol, 2-propanol and 1-butanol. Ethanol was omitted from this series because it was measured extensively in the past. Data are presented in the temperature range 220 to 500 K up to a pressure of 125 MPa. In the open literature, only scattered data were available especially at elevated temperatures and pressures as depicted in Figure 1. To strengthen the database of experimental results, precise speed of sound data with a maximum expanded uncertainty (k = 2) of up to 0.11% are reported. The present experimental results were fitted with a double polynomial equation and compared with literature data.

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2. Experiment

2.1. Materials

The fluids under investigation were purchased at high purity and used without any further purification, except for degassing the reference fluid (water) and the alcohols. Details are provided in Table 1.

2.2. Apparatus and experimental procedure

The measuring principle of the employed experimental setup was based on the pulse-echo technique, which is the most common method to measure the speed of sound of liquids and compressed gases[19]. Details of the experimental rig were already provided in our recent publications[6,20,21] so that only a short overview is given here. To bring the pulse-echo technique into practice, a piezoelectric quartz crystal with a diameter of 15 mm and a resonance frequency of 8 MHz was used as a transducer. The quartz crystal was mounted between two polished reflectors and excited electrically by sinusoidal burst signals to generate ultrasonic sound waves.

Two waves propagate in opposite directions through the sample fluid over known distances. After reflection, they interact with the quartz crystal, which also acts as a receiver of the sound waves, cf. Figure 2. The distance between quartz crystal and reflector 1 was $l_1 \approx 20$ mm and reflector 2 was $l_2 \approx 30$ mm. Because of the difference between the propagation lengths, the two echoes were received at different times t_1 and t_2, where $\triangle t = t_2 - t_1$. A high-resolution digital oscilloscope was used to monitor the timing of the echoes received by the quartz crystal. Neglecting diffraction and dispersion effects, the speed of sound was calculated by

$$w = 2(l_2 - l_1)/\triangle t. \qquad (4)$$

The acoustic path length difference of the sensor $\Delta l = l_2 - l_1$ was calibrated with pure water. It was used as a reference because it is a particularly well studied fluid[22–24] and available at very high purity. Moreover, highly precise data for the speed of sound were reported by Lin and Trusler[19] with an uncertainty of 0.04% and the reference quality equation of state by Wagner and Pruβ[25] is available. The calibration procedure and the correction of the path length variation due to temperature and pressure has been described in detail in preceding work[6]. The change in path length was considered by

$$\Delta l_{T,p} = \Delta l_{T_0,p_0}\left(1 + \alpha\left(T - T_0\right) + \frac{1}{E}\left(1 - 2\upsilon\right)\left(p_0 - p\right)\right). \qquad (5)$$

Therein, $\triangle l_{T0, p0}$ is the calibrated path length at $T_0 = 300$ K and $p_0 = 1.29$ MPa, α the linear thermal expansion coefficient, E the elastic modulus and υ the Poisson number.

Figure 3 shows that the present calibration measurements are convincingly consistent with the experimental data by Lin and Trusler[19] and the equation of state by Wagner and Pruβ.[25] The present data even show a better agreement with the reference equation of state at high pressures. All measured state points agree almost within 0.02%, except for one with a deviation of 0.05%.

Before filling the sampled fluid in to the measurement cell, it was evacuated for two hours.

3. Results and discussion

The speed of sound of the alcohols was measured for liquid and supercritical states along seven isotherms, i.e. 220 K, 250 K and with an increment of 50 K up to 500 K. The pressure was varied from 0.1 MPa up to 125 MPa for 2-propanol and three isotherms for methanol. The maximum pressure was 80 MPa

for the remaining isotherms of methanol, 1-propanol and 1-butanol because of pressure vessel leakage problems. Since there was no equation of state of high accuracy available for 1-propanol, 2-propanol and 1-butanol, a double polynomial expression suggested by Sun et al.[26] was implemented to fit the present experimental data for the alcohols

$$p - p_0 = \sum_{i=1}^{3} \sum_{j=0}^{2} a_{ij}(u - u_0)^i T^j. \qquad (6)$$

Therein, the initial pressure is $p_0 = 0.1$ MPa and u_0 is the speed of sound at p_0. The temperature dependence of u_0 was fitted with a polynomial

$$u_0 = \sum_{j=0}^{6} b_j T^j, \qquad (7)$$

where a_{ij} and b_j are coefficients that are independent of temperature and pressure. To determine the fitting quality, the average percentage deviation was calculated by

$$AAD = \frac{100}{n} \sum_{i=1}^{n} \left|\frac{w_{data} - w_{equation}}{w_{data}}\right|_i, \qquad (8)$$

where n is the number of experimental data points. Deviations of experimental literature data from equation (6) were calculated by

$$\Delta w = 100\frac{w_{data} - w_{equation}}{w_{data}}. \qquad (9)$$

To correlate present experimental data, equation (7) was fitted first to speed of sound data at p_0 to obtain the coefficients b_j and subsequently equation (6) was fitted to all speed of sound data by minimizing the quadratic sum of the difference between the experimental and calculated speed of sound. For the high temperature isotherms, i.e. 450 K and 500 K, it was not possible to measure u_0 because the alcohols are supercritical. Instead, for these high temperature isotherms, equation (6) was fitted first to these individual isotherms to estimate u_0 values, which were then used in equation (7) in an iterative way. The coefficients of equations (6) and (7) along with the AAD are provided in Table 2. The performance of equation (6) for the alcohols is presented in Figure 4, where it is shown that all experimental speed of sound data are in good agreement with the speed of sound correlation (6). For low temperature isotherms, the speed of sound increases approximately linearly with pressure. At elevated temperatures and low pressures, a rapid change of the speed of sound was observed, i.e. 450 K and 500 K and pressures below 20 MPa. This sudden drop of the speed of sound is due to the proximity to the critical point of the alcohols.

The overall expanded speed of sound measurement uncertainty $U(w)$ is composed of the relevant contributions due to standard uncertainties of temperature $u(T)$ and pressure measurements $u(p)$, as well as the uncertainty of the path length difference $u(\Delta l)$ and the uncertainty of the time measurement $u(t)$[27]

$$U(w) = k\left[\begin{array}{l}\left(\left(\frac{\partial w}{\partial T}\right)_{p,l,t} u(T)\right)^2 + \left(\left(\frac{\partial w}{\partial p}\right)_{T,l,t} u(p)\right)^2 \\ + \left(\left(\frac{\partial w}{\partial \Delta l}\right)_{p,T,t} u(\Delta l)\right)^2 + \left(\left(\frac{\partial w}{\partial t}\right)_{p,l,T} u(t)\right)^2\end{array}\right]^{\frac{1}{2}} \cdot \quad (10)$$

Assuming a coverage factor $k = 2$ leads to a level of confidence of 95%. According to the error propagation law, the total

expanded uncertainty for data on the four alcohols varies between 0.07% and 0.11%.

A more detailed uncertainty budget is provided in Table 3. It includes information on the measurement devices used in the present work, along with the influence of their individual uncertainties on the speed of sound data. The provided uncertainty of the PT-25 thermometer was assumed to be ten times larger than its actual value because it was not in a direct contact with the fluid.[6] To suppress the pressure uncertainty, three pressure transducers were used, possessing different operating ranges. Note that the sample purity was not considered in the uncertainty budget.

3.1. Results for methanol

Experimental speed of sound data for methanol with uncertainties are listed in Table 4. A comparison of the present data set, experimental literature values and the Helmholtz energy equation of state by De Reuck and Craven[28] is shown in Figure 5. An uncertainty of 2% for speed of sound values was specified by De Reuck and Craven[28] for their equation of state. The AAD of the present experimental data from equation (6) is 0.24%. Data measured by Dávila et al.[29] with AAD of 0.15% almost exactly match with the present data at 250 K and 350 K, considering their experimental uncertainty of 0.03%. They also implemented the pulse-echo technique with a sample purity of >99.9%.

Several authors reported data near 300 K exhibiting the following AAD: Plantier et al.,[30] 0.50%; Sun et al.,[31] 2.66%; Wilson and Bradley,[32] 0.76%; Carnevale and Litovitz,[33] 0.84% and Hawley et al.,[34] 6.33%. Data by Plantier et al.[30] with an uncertainty of <0.20% are in good agreement with present speed of sound values at 300 K. However, they show a systematic offset at 350 K, but the deviations are almost within the cumulative experimental uncertainty of their and the present work. Moreover, their reported sample purity >99% was lower than here. Data by Sun et al.[31] and Wilson and Bradley[32] with experimental uncertainties of <0.04% and <0.56 m s^{-1} also validate the present measurements. At some state points, data by Hawley et al.[34] and Carnevale and Litovitz[33] verify present values too, but these authors did not provide information on experimental uncertainty or sample purity.

The entire experimental dataset coincides well with equation (6), except for the data by Sun et al.[31] at 350 K. It seems that their data contain random errors at higher temperature. The equation of state by De Reuck and Craven[28] is in a very good agreement with the experimental data at 300 K, but it shows an offset for other isotherms, especially at low pressures. However, it is throughout consistent with the measured data, even for the highest isotherm, i.e. 500 K. The equation of state contains information on the critical point and numerous other thermodynamic properties such that it can represent the speed of sound data efficiently. Nonetheless, the equation of state for methanol should be improved in the liquid and supercritical region by considering the present experimental results.

3.2. Results for 1-propanol

Experimental speed of sound data for 1-propanol with uncertainties are listed in Table 5. Deviations of experimental speed of sound data from equation (6) are shown in Figure 6. To the best of our knowledge, no experimental data were published for this substance for elevated temperatures and pressures. Speed of sound data for three isotherms were compared with the available literature data and the AAD of present data from equation (6) is 0.14%. Most recent data reported by Dávila et al.[29] (AAD

= 0.07%) with an experimental uncertainty of 0.013% and a sample purity of 99.9% are in good agreement with the present data at 300 K and 350 K. Again, their data show a systematic offset at 250 K, which is within the collective experimental uncertainty of both works.

Around 300 K, speed of sound data were measured by different authors with the following AAD: Wilson and Bradley,[32] 0.17%; Marczak et al.,[5] 0.30%; Dzida and Ernst,[35] 0.27%; Carnevale and Litovitz,[33] 0.04%; Hawley et al.,[34] 3.13%; Sysoev and Otpushchennikov,[36] 4.11%; Hagelberg,[37] 12.67%. Results by Wilson and Bradley[32] with an experimental uncertainty of <0.56 m s^{-1} and a sample purity of 99.9% almost exactly match with present results. Data reported by Marczak[5] and Dzida[35] are in good agreement with present measurements, except for a single data point at 15.2 MPa. Both authors claimed an experimental uncertainty of 0.04% and a sample purity of 99.8%. Measurements by Carnevale,[33] Hagelberg[37] and Hawley[34] confirm the present data at some state points too, but no information was provided on experimental uncertainty or sample purity.

All experimental results follow more or less a similar trend in the considered temperature and pressure range, except for the data by Sysoev and Otpushchennikov.[36] Their data coincide with the other results at around 20 MPa, but the deviations are significant at higher and lower pressures. This trend can be seen most clearly for the 350 K isotherm.

3.3. Results for 2-propanol

Experimental speed of sound data for 2-propanol with uncertainties are listed in Table 6. To the best of our knowledge, only a single experimental data set at elevated pressure is available in the literature for this substance, reported by Dávila et al.[38] Deviations of experimental speed of sound data from equation (6) are presented in Figure 7. The AAD of present speed of sound values from equation (6) is 0.14%. Data reported by Dávila et al. (AAD = 0.20%) with an experimental uncertainty of 0.013% coincide with present measurements at 300 K. However, their data show a systematic offset at 250 K and 350 K. It should be noted that their claimed sample purity was 99.9%, whereas it was 99.99% here. Their data at 250 K and 350 K deviate more at low pressures and systematically approach the present results at high pressures. This behavior was not observed for the other alcohols, where their measurements follow a trend that is similar to the present work.

3.4. Results for 1-butanol

Experimental speed of sound data for 1-butanol with uncertainty values are given in Table 7. Deviations of the present experimental data from equation (6) and a comparison with experimental literature data is shown in Figure 8. Most of the authors reported data around 300 K and 350 K, only one data set was found at 253 K and 393 K. Data reported by Dávila et al.[29] (AAD = 0.09%) with an experimental uncertainty of 0.01% and a sample purity of <99.8% are in excellent agreement with the present work within their temperature range from 253 K to 353 K.

At 300 K, data published by Wilson and Bradley,[32] having an AAD of 0.15%, an experimental uncertainty of <0.56 m s^{-1} and a sample purity of 99.9%, almost exactly match with the present data at low pressure and show a systematic offset at elevated pressure. Data by Shoitov and Otpushchennikov[39] with an AAD of 0.26% and an experimental uncertainty of 0.04% also validate the present data at 350 K. Plantier et al.[30] (AAD = 0.21%) with an experimental uncertainty of <0.2% and a sample purity of <99% follow the same systematic trend along the

isotherms 300 K and 350 K. The deviations are largest around 10 MPa.

Other authors also published speed of sound data for 1-butanol, exhibiting the following AAD: Carnevale and Litovitz,[33] 0.40%; Hawley et al.,[34] 0.41%; Nematulloev et al.,[40] 1.32%; Belinskii et al.,[41] 0.74%. However these authors provided no information on experimental uncertainty or sample purity, but their data more or less validate the present results at some state points, but most of their data deviate by more than 0.7%. As the data by Sysoev et al.[42] for 1-butanol were available along other isotherms than the present work, their results were not considered for comparison.

Apart from the data by Plantier et al.[30] and Nematulloev et al.,[40] all the experimental results show a similar trend. The results by Plantier et al.[30] exhibit a different pattern at 300 K and 350 K despite the fact that their data for methanol at 300 K are in an excellent agreement with the present measurements. This behavior could be a consequence of improper degassing of the sample fluid. Data by Nematulloev et al.[40] scatter around the other experimental results, especially at 350 K, indicating large uncertainties.

A thermodynamic model developed by Safarov et al.[15] was compared with the experimental data along five isotherms. They calculated the speed of sound from density measurements of 1-butanol, showing large deviations at low temperatures, i.e. 250 K and 300 K. However, at high temperatures and pressures these data match with the present measurements at some state points. For the 450 K isotherm, their model shows a good performance.

4. Conclusion

Speed of sound data of methanol, 1-propanol, 2-propanol and 1-butanol were sampled with the pulse-echo technique in the liquid and supercritical region. The provided data along seven isotherms cover a wide temperature range from 220 K to 500 K and a pressure of up to 125 MPa, where limited or inconsistent experimental literature data were available for the alcohols. The standard measurement uncertainty is 0.02 K for temperature, 0.002 MPa for pressure below 10 MPa, 0.02 MPa for pressure between 10 MPa and 100 MPa, 0.06 MPa for pressure above 100 MPa. This amounts up to 0.11% expanded uncertainty for speed of sound values, at a confidence level of 95% ($k = 2$). A double polynomial equation was satisfactorily fitted to the speed of sound data for the alcohols. The absolute average uncertainty of experimental speed of sound data for the alcohols from their equations were 0.24%, 0.14%, 0.14% and 0.13%, respectively. The accuracy of the present data is confirmed by a detailed comparison with the available literature sources.

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Table 1. Specification of the fluids under study

fluid	CAS no.	formula	purity %	supplier
water	7732-18-5	H_2O	99.99	Merck
methanol	67-56-1	CH_3OH	≥99.9	Merck
1-propanol	71-23-8	$CH_3(CH_2)_2OH$	>99.99	Sigma-Aldrich
2-propanol	67-63-0	$(CH_3)_2CHOH$	99.99	Honeywell
1-butanol	71-36-3	$CH_3(CH_2)_3OH$	99.97	Alfa Aesar

Table 2. Coefficients of equations (6) and (7)

	methanol	1-propanol	2-propanol	1-butanol
a_{10}	2.9273035E-01	3.7240367E-01	3.4357521E-01	3.8741741E-01
a_{11}	-4.9362767E-04	-7.0452943E-04	-6.5882505E-04	-7.0483519E-04
a_{12}	-1.6073923E-15	-4.2322239E-15	1.3242749E-14	-2.3742266E-15
a_{20}	1.6571387E-03	5.4281481E-04	3.7045380E-04	2.4209078E-04
a_{21}	-6.0822729E-06	-1.2660930E-06	-8.0027071E-07	-3.4303907E-07
a_{22}	5.3172980E-09	5.6136655E-10	1.8808617E-10	1.2928960E-11
a_{30}	-2.9390275E-06	-1.5511570E-06	-3.4299590E-07	-2.6850937E-07
a_{31}	1.3705131E-08	7.3030049E-09	1.9795323E-09	1.6947649E-09
a_{32}	-1.5164299E-11	-8.2036313E-12	-2.3952863E-12	-2.1260700E-12
b_0	-2.7825023E+03	-5.7639323E+03	-6.0142996E+03	1.0472687E+03
b_1	9.4059302E+01	1.5406467E+02	1.5704867E+02	2.3934220E+01
b_2	-7.7183950E-01	-1.2413154E+00	-1.2666427E+00	-2.2274688E-01
b_3	3.1554647E-03	5.0560116E-03	5.1852877E-03	8.8233517E-04
b_4	-7.1048564E-06	-1.1305058E-05	-1.1674734E-05	-1.8391613E-06
b_5	8.4533549E-09	1.3246123E-08	1.3781109E-08	1.9543988E-09
b_6	-4.2022846E-12	-6.4022089E-12	-6.7158197E-12	-8.5207435E-13
AAD	0.24%	0.14%	0.14%	0.13%

Table 3. Uncertainty budget for the speed of sound measurements for the alcohols at a confidence level of 95% ($k = 2$)

source	type	measuring range	standard uncertainty	sensitivity coefficient[a]	relative expanded uncertainty[a] %
temperature	PT-25	84 - 693 K	0.02 K	$\partial w/\partial T$ = 2.2 m s^{-1} K^{-1}	0.007
pressure	Keller-PAA-33X	<10 MPa	0.002 MPa		
	Keller-PAA-33X	<100 MPa	0.01 - 0.02 MPa	$\partial w/\partial p$ = 4.7 m s^{-1} MPa^{-1}	0.008
	Honeywell TJE	<200 MPa	0.06 MPa		
time	handyscope HS5	-	0.002 μs	$\partial w/\partial t$ = 7.0·10^7 m s^{-2}	0.024
path length	-	-	7 μm	$\partial w/\partial \Delta l$ = 5.9·10^4 s	0.070

[a]The values are for a typical state point at 350 K and 40 MPa.

Table 4. Experimental speed of sound data for methanol at temperature T and pressure p[a]

T	p	w	$U(w)$	T	p	w	$U(w)$
K	MPa	m s^{-1}	m s^{-1}	K	MPa	m s^{-1}	m s^{-1}
220.38	0.100	1387.9	1.1	349.99	19.881	1070.5	0.8
220.41	1.023	1391.8	1.1	350.00	41.608	1186.3	0.9
220.39	1.839	1395.3	1.1	349.95	60.336	1270.3	1.0
220.96	10.454	1428.5	1.1	349.96	82.312	1356.2	1.0
220.46	20.095	1467.9	1.1	349.96	99.275	1415.9	1.1
220.39	40.357	1540.1	1.2	349.97	124.114	1495.1	1.2
220.26	60.890	1606.5	1.3	399.94	0.798	770.2	0.6
220.38	69.376	1631.5	1.3	399.94	1.015	772.5	0.6
220.37	69.581	1632.2	1.3	399.94	2.112	784.4	0.6
220.37	111.490	1746.8	1.4	399.93	5.110	815.0	0.6
244.25	0.125	1294.5	1.0	399.92	9.339	854.2	0.6
244.27	0.761	1297.5	1.0	399.92	21.337	948.3	0.7
244.28	1.200	1299.5	1.0	399.89	42.375	1078.3	0.8
244.30	1.980	1303.2	1.0	399.90	61.164	1172.4	0.9
244.31	5.110	1317.8	1.0	399.91	81.158	1258.6	0.9
244.32	9.712	1338.5	1.0	399.93	84.741	1273.4	1.0
299.95	0.099	1096.3	0.8	399.73	98.358	1325.1	1.0
299.94	0.963	1101.7	0.8	399.91	122.977	1409.6	1.1
299.94	2.240	1109.5	0.8	450.22	2.562	568.3	0.5
299.95	5.128	1126.7	0.8	450.19	4.910	608.8	0.5
299.95	9.896	1153.8	0.9	450.22	14.312	730.4	0.6
299.96	21.093	1212.5	0.9	450.20	20.347	794.1	0.6
299.96	40.780	1302.9	1.0	450.18	39.568	943.1	0.7
299.95	58.877	1375.6	1.0	450.17	59.905	1062.6	0.8
299.94	80.229	1452.1	1.1	450.20	72.355	1124.9	0.8
299.95	98.460	1511.3	1.2	500.06	9.535	412.8	0.4
299.96	123.414	1585.5	1.3	499.98	19.828	611.1	0.5
349.98	0.201	935.8	0.7	499.94	28.092	708.5	0.6
349.98	0.970	941.9	0.7	500.06	30.612	733.2	0.6
349.98	1.998	949.9	0.7	499.94	40.326	818.5	0.6
349.98	4.864	971.5	0.7	499.94	60.313	955.4	0.7
349.97	9.858	1006.8	0.7				

[a]The expanded uncertainties $U(w)$ for 0.95 level of confidence ($k = 2$) were calculated by considering the standard uncertainties: $u(T) = 0.02$ K, $u(\triangle l) = 7$ μm, $u(t) = 0.002$ μs; for the pressure measurements, three pressure sensors were used with different operating ranges possessing the following $u(p)$ values: 0.002 MPa for $p < 10$ MPa, 0.02 MPa for $p < 100$ MPa, and 0.06 MPa for $p \geq 100$ MPa.

Table 5. Experimental speed of sound data for 1-propanol at temperature T and pressure p^a

T	p	w	$U(w)$	T	p	w	$U(w)$
K	MPa	m s^{-1}	m s^{-1}	K	MPa	m s^{-1}	m s^{-1}
218.20	0.102	1512.0	1.2	350.08	20.259	1164.3	0.9
218.26	0.875	1515.2	1.2	350.04	40.537	1273.0	1.0
218.21	2.111	1520.8	1.2	350.03	52.186	1327.6	1.0
218.26	5.018	1533.1	1.2	350.04	60.588	1364.3	1.0
218.32	9.465	1551.0	1.2	400.05	0.307	847.6	0.6
218.35	19.810	1591.6	1.2	400.05	0.947	854.9	0.6
218.34	29.071	1626.6	1.3	400.05	2.155	867.0	0.6
218.31	49.499	1698.1	1.3	400.03	4.879	893.3	0.7
218.32	61.345	1736.4	1.4	400.07	9.768	936.6	0.7
249.99	0.100	1382.6	1.1	400.07	19.974	1015.3	0.8
249.99	0.177	1383.0	1.1	400.06	27.823	1068.3	0.8
249.99	1.128	1387.7	1.1	399.98	30.784	1087.2	0.8
250.01	2.296	1393.4	1.1	399.96	40.232	1142.9	0.9
249.97	5.362	1408.3	1.1	399.98	50.284	1196.8	0.9
249.94	9.322	1427.1	1.1	399.97	59.616	1242.9	0.9
249.90	20.903	1478.7	1.1	450.12	1.081	636.4	0.5
249.93	39.564	1553.9	1.2	450.12	2.181	653.9	0.5
249.94	59.448	1625.8	1.3	450.11	5.172	697.0	0.5
299.97	0.138	1199.6	0.9	450.11	9.782	754.2	0.6
299.96	1.174	1206.0	0.9	450.10	20.385	860.0	0.7
299.96	2.560	1214.3	0.9	450.11	30.113	938.6	0.7
299.98	5.042	1228.8	0.9	450.13	40.189	1008.7	0.8
299.98	9.515	1254.1	0.9	450.13	50.091	1069.5	0.8
299.96	19.849	1308.7	1.0	500.31	4.798	438.4	0.4
299.96	39.521	1400.6	1.1	500.32	9.558	542.3	0.4
299.96	49.960	1444.6	1.1	500.32	19.968	690.2	0.6
350.05	0.270	1030.8	0.8	500.31	30.851	799.1	0.6
350.07	0.997	1036.3	0.8	500.28	39.800	870.0	0.7
350.07	2.073	1044.4	0.8	500.30	50.346	946.6	0.7
350.07	5.244	1067.5	0.8	500.31	60.509	1009.7	0.8
350.06	9.697	1098.3	0.8	500.31	77.533	1102.4	0.8

^{a}The expanded uncertainties $U(w)$ for 0.95 level of confidence ($k = 2$) were calculated by considering the standard uncertainties: $u(T) = 0.02$ K, $u(\triangle l) = 7$ μm, $u(t) = 0.002$ μs; for the pressure measurements, three pressure sensors were used with different operating ranges possessing the following $u(p)$ values: 0.002 MPa for $p < 10$ MPa, and 0.02 MPa for $p < 100$ MPa.

Table 6. Experimental speed of sound data for 2-propanol at temperature *T* and pressure *p*[a]

T	*p*	*w*	*U*(*w*)	*T*	*p*	*w*	*U*(*w*)
K	MPa	m s⁻¹	m s⁻¹	K	MPa	m s⁻¹	m s⁻¹
217.77	0.143	1445.1	1.1	349.97	1.915	966.0	0.7
217.84	1.031	1449.0	1.1	349.97	5.044	992.5	0.7
217.84	2.256	1454.8	1.1	349.97	9.682	1029.2	0.8
217.88	6.084	1472.2	1.1	349.98	21.490	1111.7	0.8
217.00	8.951	1489.1	1.1	349.98	42.396	1232.7	0.9
216.95	24.689	1556.1	1.2	349.97	61.179	1324.0	1.0
216.87	41.140	1619.7	1.3	349.97	81.377	1409.9	1.1
216.89	60.566	1688.1	1.3	349.97	96.752	1469.0	1.1
216.90	78.557	1746.2	1.4	349.94	123.510	1562.0	1.3
216.97	98.400	1805.5	1.4	399.64	0.492	745.0	0.6
216.96	121.241	1868.7	1.5	399.63	1.090	752.7	0.6
249.84	0.159	1317.8	1.0	399.63	1.986	764.1	0.6
249.86	0.992	1322.3	1.0	399.62	5.275	802.7	0.6
249.87	2.039	1328.0	1.0	399.62	9.782	850.0	0.6
249.85	4.937	1343.6	1.0	399.61	20.985	948.9	0.7
249.85	9.128	1365.3	1.0	399.63	38.384	1071.2	0.8
249.86	10.803	1373.6	1.1	399.63	61.965	1203.3	0.9
249.85	19.905	1417.6	1.1	399.61	80.647	1291.3	1.0
249.85	41.768	1512.2	1.2	399.60	97.607	1362.4	1.0
249.85	59.235	1579.4	1.2	399.66	122.092	1454.2	1.2
249.85	80.375	1653.1	1.3	450.06	1.639	499.2	0.4
249.85	96.644	1705.5	1.3	450.04	2.190	512.0	0.4
249.85	124.462	1787.6	1.5	450.02	22.115	792.1	0.6
299.79	0.086	1132.8	0.8	449.97	42.419	957.3	0.7
299.80	0.865	1138.2	0.9	449.98	61.580	1076.2	0.8
299.81	2.097	1146.6	0.9	449.99	82.381	1183.6	0.9
299.81	5.133	1166.5	0.9	450.00	97.646	1252.6	0.9
299.79	9.677	1195.1	0.9	450.00	122.429	1352.4	1.1
299.80	20.194	1256.1	1.0	500.17	7.568	371.1	0.3
299.80	39.488	1353.7	1.0	500.15	9.582	424.0	0.3
299.81	60.935	1447.1	1.1	500.11	22.653	636.6	0.5
299.89	81.993	1527.9	1.2	500.25	40.483	812.4	0.6
299.88	97.237	1581.4	1.2	500.27	61.769	961.8	0.7
299.85	123.509	1665.9	1.4	500.27	80.461	1067.0	0.8
349.93	0.138	950.4	0.7	500.27	98.305	1153.8	0.9
349.94	1.099	958.9	0.7	500.28	123.715	1261.3	1.1

[a]The expanded uncertainties *U*(*w*) for 0.95 level of confidence (*k* = 2) were calculated by considering the standard uncertainties: *u*(*T*) = 0.02 K, *u*(△*l*) = 7 μm, *u*(*t*) = 0.002 μs; for the pressure measurements, three pressure sensors were used with different operating ranges possessing the following *u*(*p*) values: 0.002 MPa for *p* < 10 MPa, 0.02 MPa for *p* < 100 MPa, and 0.06 MPa for *p* ≥ 100 MPa.

Table 7. Experimental speed of sound data for 1-butanol at temperature T and pressure p[a]

T	p	w	$U(w)$	T	p	w	$U(w)$
K	MPa	m s⁻¹	m s⁻¹	K	MPa	m s⁻¹	m s⁻¹
218.17	0.100	1536.6	1.2	350.11	20.660	1199.6	0.9
218.25	1.111	1540.5	1.2	350.10	40.651	1303.9	1.0
218.26	2.129	1544.8	1.2	350.10	59.555	1388.7	1.1
218.31	5.399	1558.2	1.2	350.09	80.590	1472.2	1.1
218.28	9.570	1575.2	1.2	400.14	0.145	891.2	0.7
218.22	19.695	1614.9	1.3	400.14	0.933	898.8	0.7
217.92	39.005	1685.4	1.3	400.14	1.839	907.3	0.7
218.12	59.881	1753.2	1.4	400.14	4.864	934.6	0.7
218.18	79.839	1813.2	1.4	400.12	9.483	973.3	0.7
250.00	0.067	1411.8	1.1	400.14	20.722	1055.9	0.8
249.99	0.100	1412.0	1.1	400.14	36.029	1150.7	0.9
249.99	2.060	1421.4	1.1	400.14	59.027	1269.1	1.0
249.99	5.075	1435.7	1.1	400.14	79.223	1357.8	1.0
249.98	9.057	1453.9	1.1	449.96	0.576	696.4	0.5
249.98	22.437	1511.7	1.2	449.96	1.176	704.8	0.5
250.01	40.124	1581.1	1.2	449.96	2.010	716.0	0.5
249.98	58.985	1648.4	1.3	449.96	9.527	803.9	0.6
249.98	79.282	1714.5	1.4	449.96	21.165	910.4	0.7
300.04	0.101	1234.1	0.9	449.96	39.912	1043.3	0.8
300.03	1.100	1240.0	0.9	449.96	59.899	1156.8	0.9
300.03	2.196	1246.4	0.9	449.96	79.678	1251.8	0.9
300.03	5.369	1264.5	1.0	499.96	1.636	472.8	0.4
300.03	9.681	1288.1	1.0	499.96	2.336	490.0	0.4
300.03	20.060	1341.4	1.0	499.96	4.923	544.0	0.4
300.03	40.032	1432.5	1.1	499.96	7.243	586.7	0.4
300.02	59.057	1509.0	1.2	499.96	9.870	626.9	0.5
300.02	79.463	1582.8	1.2	499.95	19.314	741.4	0.6
350.11	0.104	1067.1	0.8	499.91	25.968	806.2	0.6
350.11	0.911	1073.1	0.8	499.95	40.048	918.1	0.7
350.11	2.067	1081.4	0.8	499.96	60.162	1045.7	0.8
350.11	4.569	1099.0	0.8	499.96	80.004	1149.3	0.9
350.11	9.077	1129.2	0.8				

[a]The expanded uncertainties $U(w)$ for 0.95 level of confidence ($k = 2$) were calculated by considering the standard uncertainties: $u(T) = 0.02$ K, $u(\triangle l) = 7$ μm, $u(t) = 0.002$ μs; for the pressure measurements, three pressure sensors were used with different operating ranges possessing the following $u(p)$ values: 0.002 MPa for $p < 10$ MPa, and 0.02 MPa for $p < 100$ MPa.
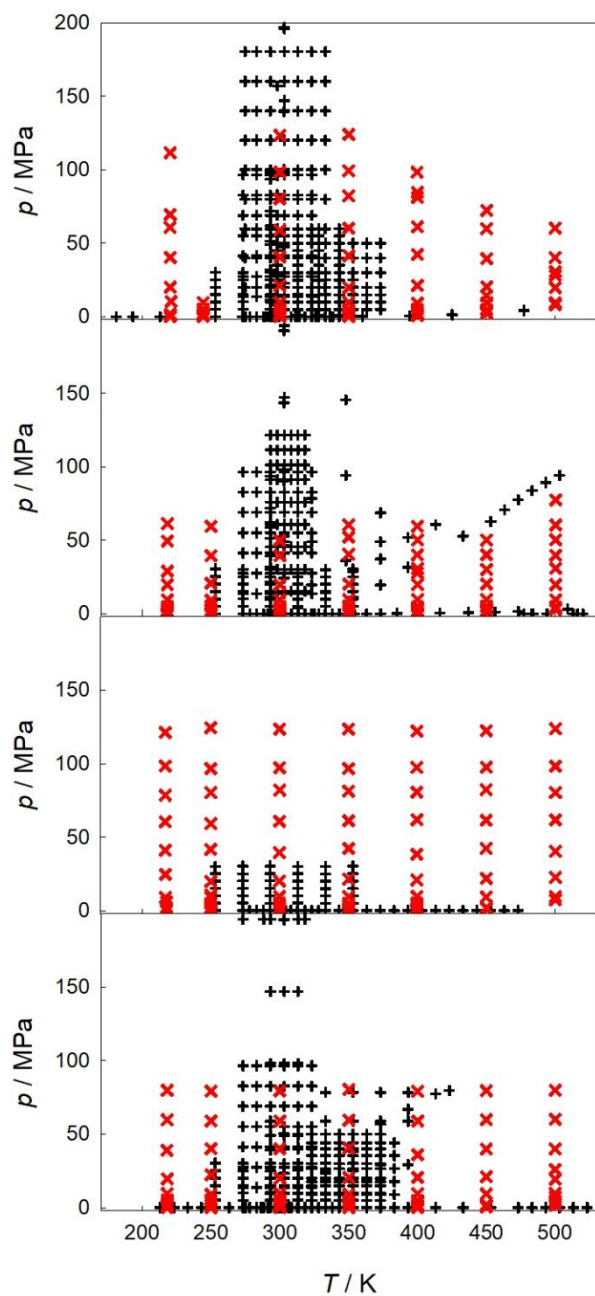
Figure 1. State points where speed of sound data were measured in this work × in comparison with experimental literature data +; from top to bottom: methanol, 1-propanol, 2-propanol, 1-butanol. Note that experimental literature data for 1-propanol and 1-butanol exist up to a pressure above 200 MPa around 300 and 350 K.
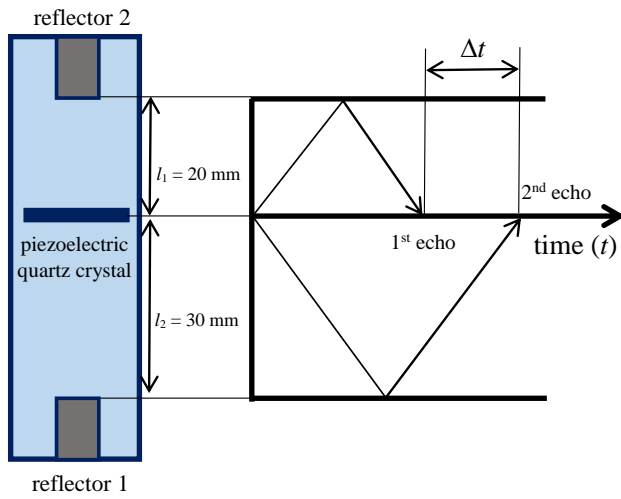
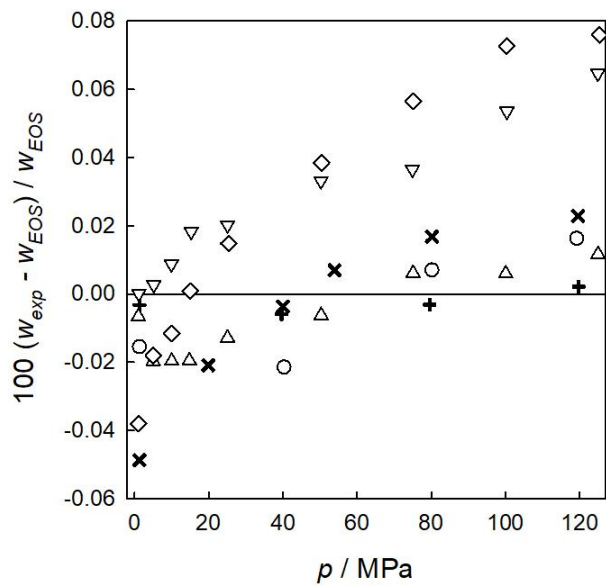**Figure 2**. Measurement principle of the pulse-echo technique based on the single wave approach.

Figure 3. Deviation of experimental speed of sound data for water from the equation of state by Wagner and Pruβ,[25] experiment, this work: ○ 300 K, + 350 K, × 400 K, experimental literature data by Lin and Trusler:[19] △ 303 K, ▽ 373 K, ◇ 413 K.
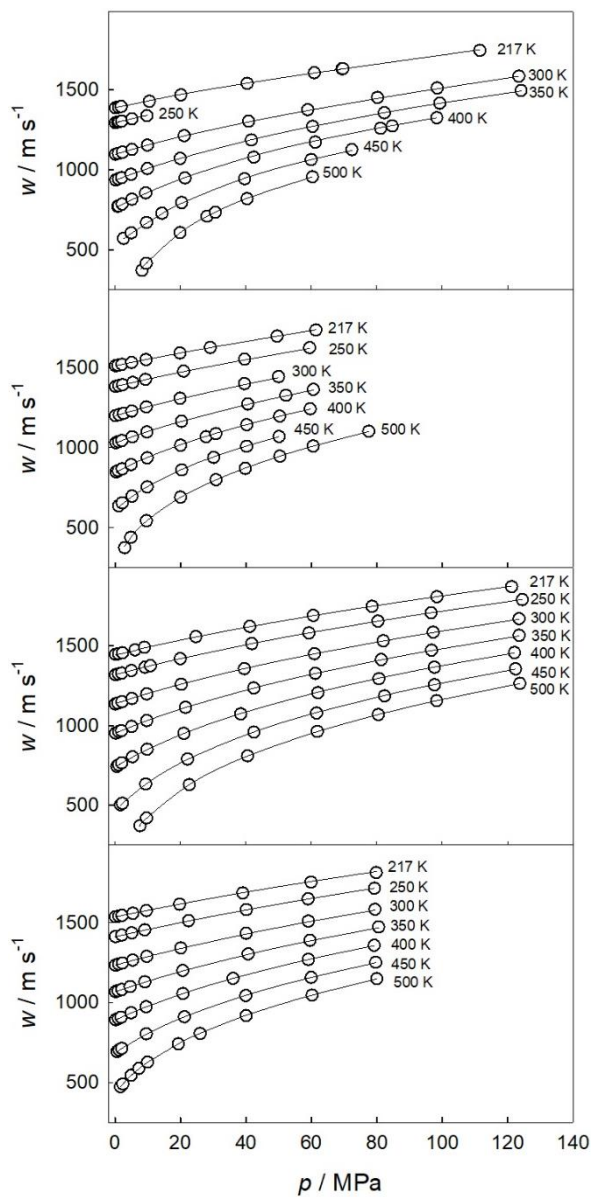
Figure 4. Speed of sound of the alcohols as a function of pressure along different isotherms: ○ experiment, this work, ▬ equation (6); from top to bottom: methanol, 1-propanol, 2-propanol, 1-butanol.
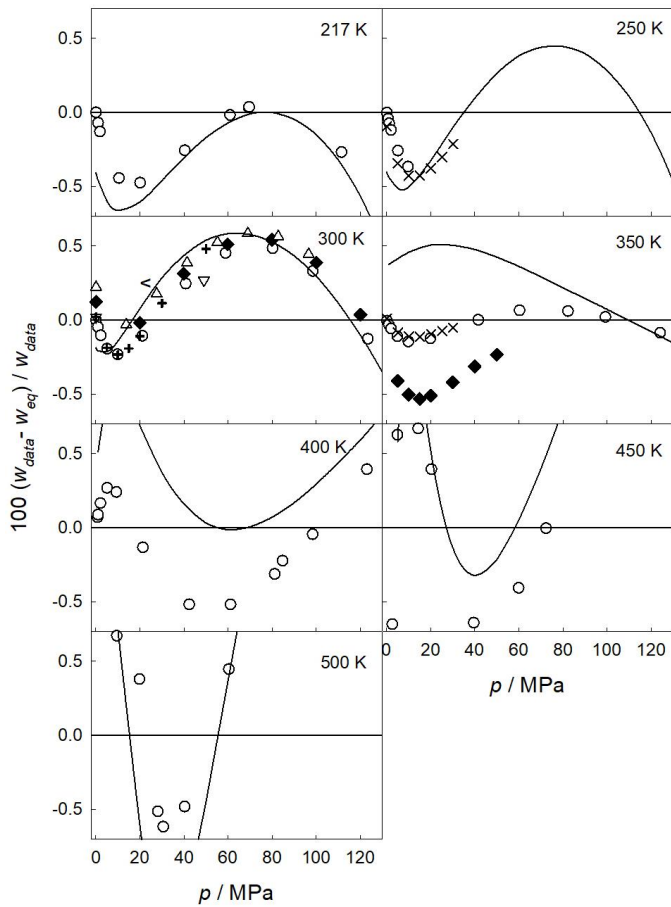
Figure 5. Deviation of speed of sound data from equation (6) for methanol: ○ experiment, this work, ━ equation of state by De Reuck and Craven,[28] experimental literature data: × Dávila et al.,[29] + Plantier et al.,[30] ♦ Sun et al.,[31] △ Wilson and Bradley,[32] ▽ Carnevale and Litovitz,[33] < Hawley et al.[34]
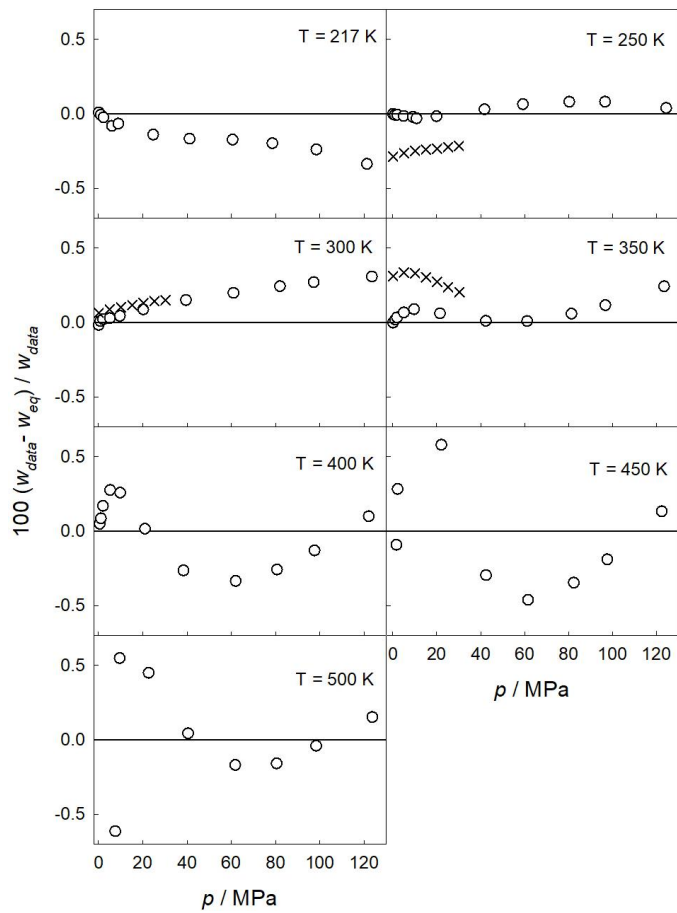
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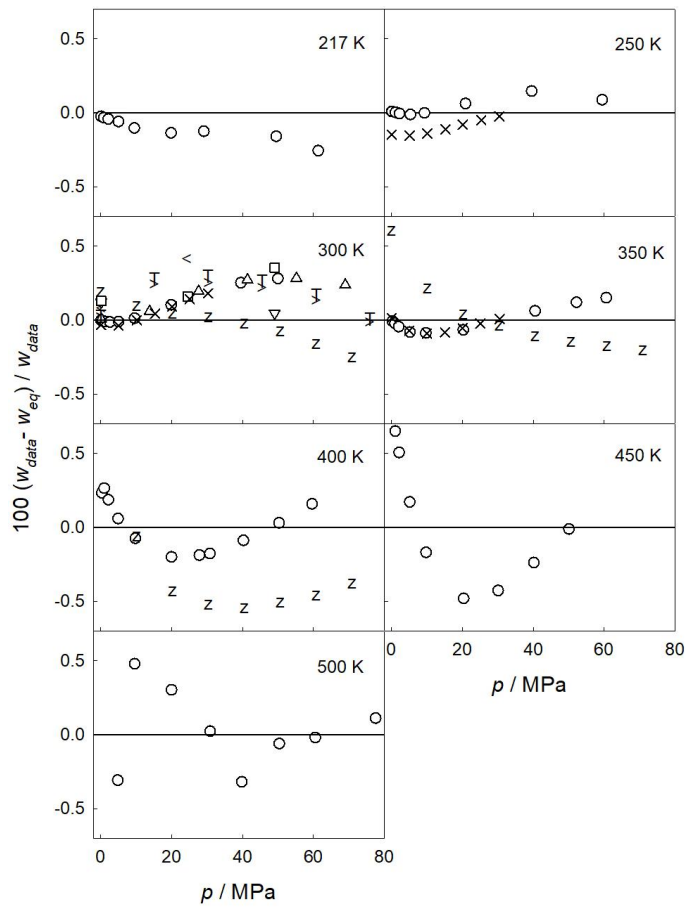
Figure 6. Deviation of speed of sound data from equation (6) for 1-propanol: ○ experiment, this work, experimental literature data: × Dávila et al.,[29] △ Wilson and Bradley,[32] ▽ Carnevale and Litovitz,[33] < Hawley et al.,[34] ⊤ Marczak et al.,[5] > Dzida and Ernst,[35] □ Hagelberg,[37] Z Sysoev and Otpushchennikov.[36]

Figure 7. Deviation of speed of sound data from equation (6) for 2-propanol: ○ experiment, this work, experimental literature data: × Dávila et al.[38]
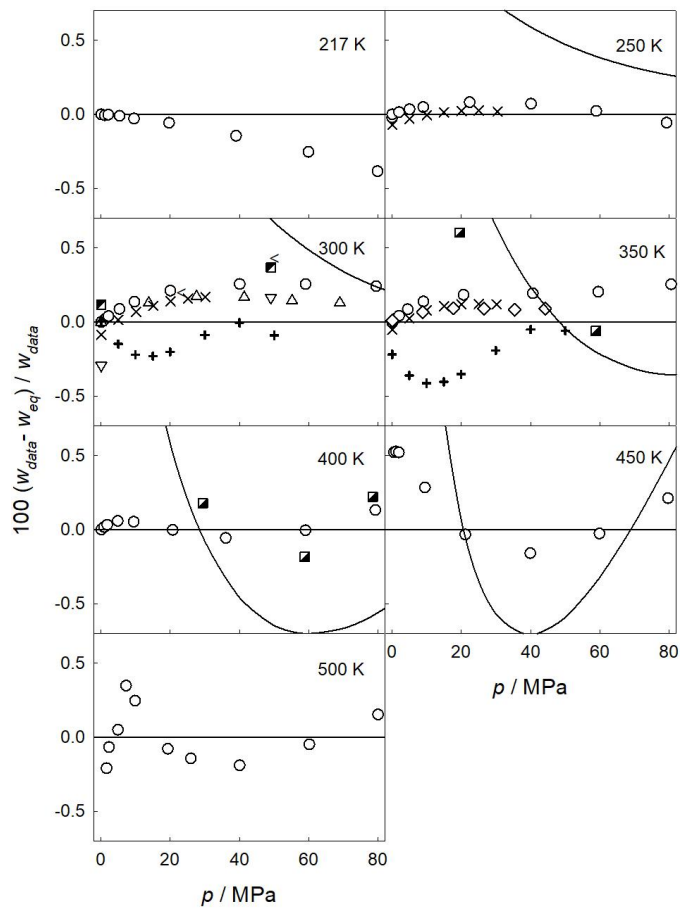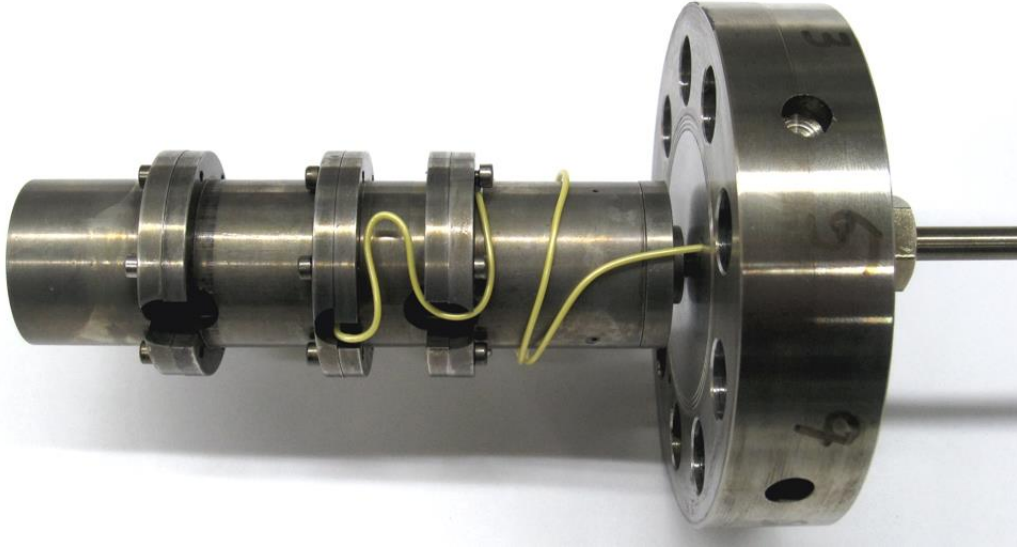
Figure 8. Deviation of speed of sound data from equation (6) for 1-butanol: ○ experiment, this work, ▬ calculated speed of sound by Safarov et al.,[15] experimental literature data: × Dávila et al.,[29] + Plantier et al.,[30] △ Wilson and Bradley,[32] ▽ Carnevale and Litovitz,[33] < Hawley et al.,[34] ◇ Shoitov and Otpushchennikov,[39] ◪ Nematulloev et al.,[40] ◩ Belinskii et al.[41]

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