Apparatus for the measurement of the thermodynamic speed of sound of diethylene glycol and triethylene glycol

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Abstract

The speed of sound is a thermodynamic equilibrium property which relates pressure to density variations at constant entropy. Because of its thermal and caloric nature, thermodynamic speed of sound data are crucial for the parametrization of highly accurate Helmholtz energy equations of state, which are in great demand. In the present work, the thermodynamic speed of sound of diethylene glycol and triethylene glycol is measured with an apparatus based on the pulse-echo technique. The measurements are performed along five isotherms covering a temperature range between 300 K and 500 K, while the pressure was varied from 0.1 MPa to 45 MPa. The maximum relative expanded uncertainty of the reported data is 0.11% for both glycols. A double polynomial

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equation is fitted to the present data with a maximum deviation of 0.2% for diethylene glycol and 0.04% for triethylene glycol. A comprehensive comparison with literature data is carried out, confirming the present data at ambient conditions. However, for high temperature isotherms, deviations are up to 2% for diethylene glycol and up to 3% for triethylene glycol.

Introduction

Glycols are organic compounds that are commonly used as raw materials in the polymer industry. They are attractive industrial fluids because of their high boiling point, freezing point depression, hygroscopicity, non-corrosiveness, as well as lubricating, plasticizing and solvent properties. They are used in the production of inks and dyes, as process solvents in hydrocarbon purification, coolants in automobiles and coupling agents in the formation of textile lubricants. Further, the presence of hydroxyl end groups in their molecular structure makes them popular intermediates during the formation of esters.

Diethylene glycol occurs as an intermediate in the preparation of unsaturated polyester resins, polyurethanes and plasticizers. Both diethylene glycol and triethylene glycol also have applications in natural gas processing and are employed as dehydrating agents. Moreover, triethylene glycol is utilized as a dehumidifier in air-conditioning systems, as a vinyl plasticizer and is an intermediate in the formation of polyester resins or polyols.[1]

The development of technologies and the demand for new products compel industries to continuously modify and optimize their processes. For this purpose, accurate thermodynamic properties of the involved fluids are required. The speed of sound is a thermodynamic property, which is crucial for the parameterization of highly accurate Helmholtz energy equations of state. From such equations, all thermodynamic properties can be obtained.[2,3] Due

to its thermal and caloric nature that is outlined in Ref.,[4] the speed of sound is particularly suitable for the parameterization of such models. Currently, only insufficient speed of sound data are available for diethylene glycol and triethylene glycol so that no such models exist for these fluids.

Measurements of the thermodynamic speed of sound of diethylene glycol and triethylene glycol were reported in several publications, details on the number of data points and covered temperature and pressure ranges are listed in Tables 1 and 2. All authors have measured the speed of sound of these glycols only at ambient pressure, except for four state points along the saturated liquid line up to 0.4 MPa. The phase diagrams in Figure 1 depict the state points where literature data are available.

The speed of sound of diethylene glycol and triethylene glycol was measured in this work by implementing a double path length pulse-echo technique. Five isotherms in the liquid state from 300 K to 500 K with an increment of 50 K were measured, covering pressures up to 45 MPa. A detailed experimental uncertainty analysis reveals that the experimental data for both glycols have a maximum relative expanded uncertainty of 0.11% at a confidence level of 95% ($k = 2$) for the entire measurement range. Because no accurate equations of state were available, a double polynomial equation proposed by Sun et al.[5] was fitted to the present data with a relative absolute average deviation of 0.043% for diethylene glycol and 0.008% for triethylene glycol. A comparison of the present data with literature data at ambient pressure shows that the measurements reported by Kishimoto and Nomoto[6] and Willard[7] verify the present data for diethylene glycol. Data by Sastry et al.[8] and Kishimoto and Nomoto[6] are also in very good agreement with the present data for triethylene glycol. However, other authors reported data that deviate by up to 2% for diethylene glycol and up to 3% for triethylene glycol.

Table 1: Sources of experimental speed of sound data for diethylene glycol, where n is the number of measured data points, $T_{\min} - T_{\max}$ the temperature range, $p_{\max}$ the maximum pressure and U_w the measurement uncertainty, if given.

author	year	n	$T_{\min}$- $T_{\max}$/K	$p_{\max}$/MPa	U_w/m s^{-1}
Willard[7]	1947	1	298	0.1	3.3
Kishimoto and Nomoto[6]	1954	6	283 - 308	0.1	3.3
Marks[9]	1967	1	273	0.1	—
Zotov and Shoitov[10]	1970	19	293 - 473	0.4	0.2
Aminabhavi and Gopalakrishna[11]	1995	1	298	0.1	—
Sastry and Patel[12]	2003	2	298 - 308	0.1	1.3
George and Sastry[13]	2004	6	298 - 348	0.1	—
Mehta et al.[14]	2004	1	303	0.1	—
Sastry et al.[8]	2008	2	298 - 308	0.1	—
Ćwiklińska et al.[15]	2008	1	298	0.1	—
Tsierkezos and Palaiologou[16]	2009	1	298	0.1	—
Carvalho et al.[17]	2015	10	283 - 343	0.1	—
Ali et al.[18]	2015	4	298 - 313	0.1	—
Klimaszewski et al.[19]	2016	7	288 - 318	0.1	—
Hoga et al.[20]	2018	4	293 - 308	0.09	—
this work	2021	44	300 - 500	45	1.5

Table 2: Sources of experimental speed of sound data for triethylene glycol, where n is the number of measured data points, $T_{\min} - T_{\max}$ the temperature range, $p_{\max}$ the maximum pressure and U_w the measurement uncertainty, if given.

| author	year	n	$T_{\min}$- $T_{\max}$/K	$p_{\max}$/MPa	U_w/m s^{-1}
Willard[7]	1947	1	298	0.1	—
Kishimoto and Nomoto[6]	1954	5	273 - 303	0.1	3.3
Marks[9]	1967	1	273	0.1	—
Sastry and Patel[12]	2003	2	298 - 308	0.1	1.3
George and Sastry[13]	2004	6	298-348	0.1	—
Mehta et al.[14]	2004	1	303	0.1	—
Sastry et al.[8]	2008	2	298 - 308	0.1	—
Ćwiklińska et al.[15]	2008	1	298	0.1	—
Tsierkezos and Palaiologou[16]	2009	1	298	0.1	—
Carvalho et al.[17]	2015	10	283 - 343	0.1	—
Klimaszewski et al.[21]	2015	14	288 - 318	0.1	—
Hoga et al.[20]	2018	4	293 - 308	0.09	—
this work	2021	45	300 - 500	45	1.5
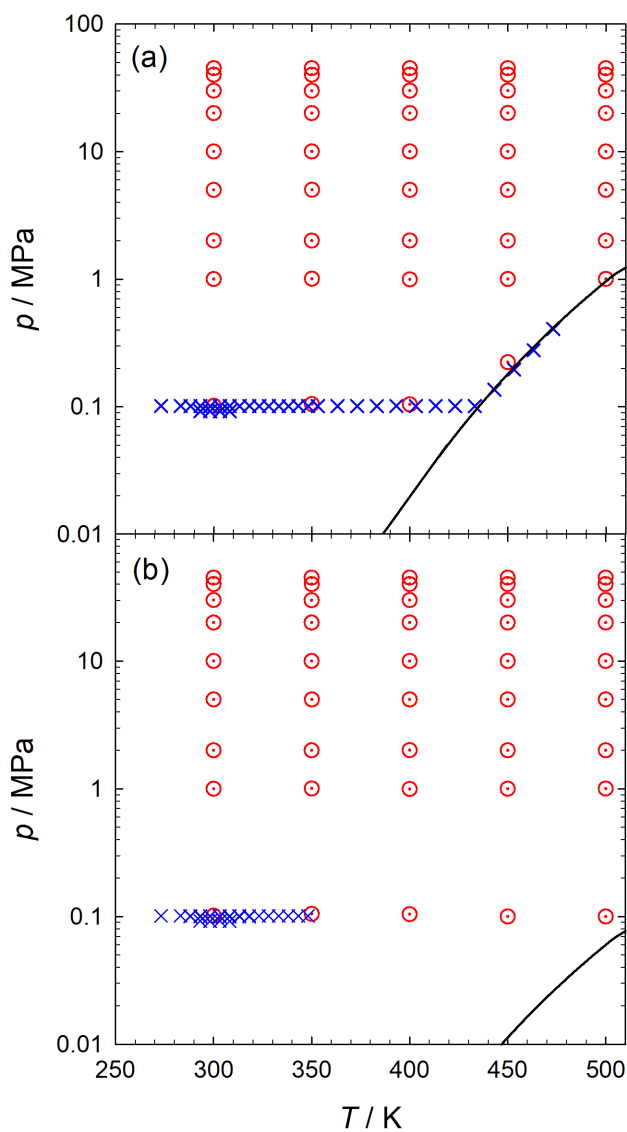
Figure 1: State points where the speed of sound of diethylene glycol (a) and triethylene glycol (b) was measured: ⊙ this work, × experimental literature data. The solid line is the relevant part of the vapor pressure curve.

Experiment

Materials

Diethylene glycol and triethylene glycol were sampled with an apparatus based on the pulse-echo technique to measure the thermodynamic speed of sound. Highly pure water was used as a calibration fluid. The liquids, their suppliers, purities and water content are listed in Table 3. Water content in diethylene glycol and triethylene glycol was provided by the supplier, which was analyzed with a coulometric titrator. It is well established that even traces of impurities may have a large impact on the thermodynamic properties. To mitigate this risk, the glycols were degased after purchase to remove volatile components, which would not alter the water content. This was achieved by keeping the glycols under vacuum for about 2 h before imbibing them into the acoustic cell.

Table 3: Suppliers along with mass fraction purity y and water content of the samples as provided by the suppliers.

name	chemical formula	CAS number	supplier	y	water content mass fraction[a]
water	H_2O	7732-18-5	Merck	0.9999	-
diethylene glycol	$(HOCH_2CH_2)_2O$	111-46-6	Sigma-Aldrich	0.9998	0.0002
triethylene glycol	$HO(CH_2CH_2O)_2CH_2CH_2OH$	112-27-6	Sigma-Aldrich	0.9970	0.0003

[a] Water content mass fraction provided by the supplier, which was analyzed with a coulometric titrator.

Apparatus

For measuring the thermodynamic speed of sound of the glycols, the pulse-echo technique was employed. With this approach, a piezoelectric quartz crystal was placed between two metallic reflectors mounted at different distances. The quartz was excited electrically such that two sound waves propagated in opposite directions through the fluid and, after reflection, were received by the quartz again. The speed of sound was derived by measuring the time difference Δt between the two echoes with the peak-to-peak measurement approach explained

by Javed et al.[3] Neglecting dispersion effects, the speed of sound w was calculated by

$$w = \frac{2\Delta L}{\Delta t},\tag{1}$$

where ΔL is the path length difference of the two reflectors. While measuring the speed of sound, diffraction effects were neglected because these corrections would amount to less than 0.01% of the time difference.[22,23] Moreover, calculating differences in transient time, diffraction and electronic delay errors should be suppressed by cancellation.[22]

Design

The design and setup of the speed of sound apparatus is depicted in Figure 2. For generating the pulse, a piezoelectric quartz crystal disc (A) was positioned inside the measuring cell between the two reflectors. The quartz disc had a diameter of 15 mm and was mounted to the measuring cell with steel clamps. Two electrodes supplied the voltage to stimulate the quartz at its operating frequency of 8 MHz.

The measuring cell (B) itself consisted of the two reflectors positioned at lengths $L_1 \approx$ 30 mm above and $L_2 \approx$ 20 mm beneath the quartz as well as one bracket which connects the cell to the pressure vessel. The components were made of 1.4571 stainless steel. The measurement cell was mounted on the closure of the pressure vessel. This offers the advantage of attaching the measurement cell to the closure first and subsequently assembling the closure and the cylinder of the pressure vessel.

The pressure vessel (C) was made of 1.4462 stainless steel and had an internal diameter of 50 mm and an external diameter of 100 mm, thus having a wall thickness of 25 mm. The flange was sealed with a copper seal. Filling and purging of the cell was done via an eccentric drilling hole in the flange, which also served as feed through for a wire connecting the quartz. Evacuation of the pressure vessel was done via the eccentric drilling at the bottom as well as the additional centered drilling at the top.

The pressure vessel was embedded inside an inner copper heater (D). The direct contact to that heating unit enabled heat transport by thermal conduction. It was placed inside a rack with glass-insulated feet (G) to minimize heat loss. To reduce heat loss by radiation, the inner copper heater was surrounded by an outer copper heater (E). The base plate (F) of the outer heater was placed on PTFE-insulated feet (J). Additionally, a heat shield (I) was installed beneath the base plate (F) to minimize thermal radiation in this direction to protect the electrical wiring. The cylindrical parts of both copper heaters (D, E) as well as the base plate of the outer heater (F) were equipped with three additional electrical heating elements (H1, H2, H3) with a power of up to 200 W each.

All components were placed inside a vacuum chamber (K) to avoid heat transport via convection. The vacuum chamber was fixed to the ground plate (L) of the apparatus and sealed with rubber. The entire apparatus was mounted on a rack made of aluminum profiles. Wiring, piping and a platinum resistance thermometer (Pt25) were inserted via vacuum feedthroughs.

Evacuation of the apparatus was done with a vacuum pump (R). Upstream of the vacuum pump, a cooling trap (P) condensed remaining vapor when purging the measuring cell. Nitrogen (Q) was used for purging. The sample vessel (N) supplied the liquid sample into the measuring cell. The pressure inside the measuring cell was adjusted by a hand spindle pump (M).

Measurement equipment

Five platinum resistance thermometers with a nominal resistance of 100 Ω were used to measure the temperature of the heaters (Pt1 to Pt5), their placement is shown in Figure 2. A sixth Pt-100 thermometer (Pt6) was used for safety reasons to switch the heaters off in case of runaway temperatures in the pressure vessel. Pt1, Pt2, Pt4 and Pt5 were connected via a switch (7) to the resistance measuring device (6), resulting in a periodical temperature measurement. Instead, Pt3 was directly connected to the resistance measuring device (5)

because it delivered the actual value for temperature control.

Since the temperature inside the measuring cell was one of the two major controlled variables (the other being the pressure), its measurement had to be highly accurate. Therefore, a calibrated platinum resistance thermometer with a nominal resistance of 25 Ω was used for this purpose. This Pt-25 was inserted into the mantle of the pressure vessel. In the steady state, temperature of the mantle is identical with that of the liquid sample inside the measuring cell due to thermodynamic equilibrium. The data delivered by all resistance measuring devices were processed with a personal computer (PC) and turned into temperature values required for controlling the system.

Pressure measurement was done with three transducers (PI1, PI2, PI3). PI1 and PI2 measured the absolute pressure inside the pressure vessel with different measurement ranges. This offered better measurement accuracy by switching between PI1 and PI2. The values were relayed to the PC. The state of the vacuum inside the chamber was monitored by a local pressure transducer (PI3).

Temperature control

To allow for a measurement along isotherms, the temperature inside the measuring cell needed to be controlled during operation. This was achieved by adjusting the voltage of the power supply of the heating elements of the inner copper heater. For this purpose, a virtual PID controller was implemented in the according software. Pt3 delivered the actual value for that process. Controlling the temperature of the outer copper heater and its base-plate was done analogously.
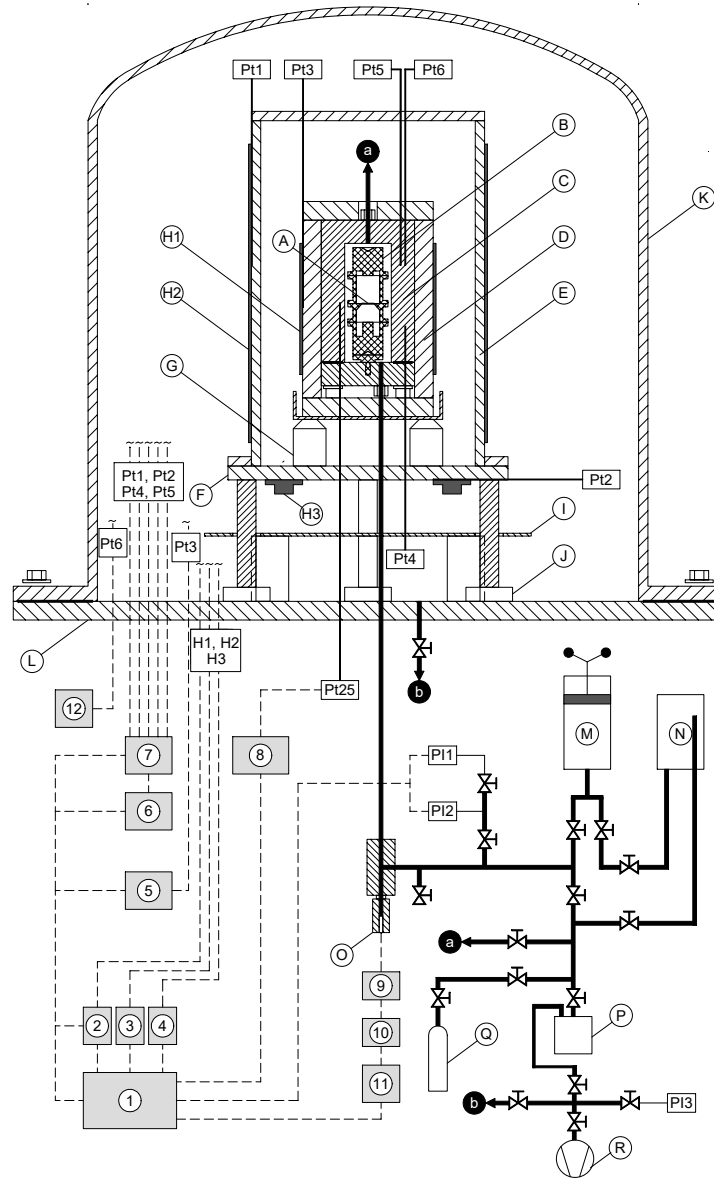
Figure 2: Schematic of the speed of sound apparatus. *Hardware components:* A. Quartz; B. Measuring cell; C. Pressure vessel; D. Inner copper heater; E. Outer copper heater; F. Outer copper heater base plate; G. Plastic insulated stand; H1-H3. Electrical heating elements; I. Heat shield; J. Plastic insulation; K. Vacuum chamber; L. Ground plate; M. Hand spindle pump; N. Test liquid vessel; O. Electrical feedthrough; P. Cooling trap; Q. Nitrogen gas cylinder; R. Vacuum pump. *Sensors:* Pt1-Pt6. Platinum resistance thermometers (100 Ω); Pt25. Platinum resistance thermometer (25 Ω); PI1-PI3. Pressure transducers. *Measurement and electrical equipment:* 1. Measuring PC; 2-4. Power supply for H1-H3; 5. Resistance measuring device for Pt3; 6. Resistance measuring device for Pt1, Pt2, Pt4, Pt5; 7. Switch for Pt1, Pt2, Pt4, Pt5; 8. Resistance measuring device for Pt25; 9. Changeable inductivity; 10. Switch for oscilloscope; 11. Oscilloscope and signal generator; 12. Controller for Pt6.

Calibration

The acoustic path length difference $\Delta L(T_0, p_0) = 9.875$ mm was calibrated with water at the state point $T_0 = 300$ K and $p_0 = 0.1$ MPa. Water was chosen as a reference fluid because of the availability of the highly precise reference quality equation of state by Wagner and Pruß[24] with an uncertainty of 0.005% for the speed of sound at the specified state point. Moreover, at ambient temperature, very accurate speed of sound measurements were reported by several authors,[25–28] which were used for validation of the present calibration.

The variation of the path length difference due to thermal expansion and pressure compression was considered by[4]

$$\Delta L(T, p) = \Delta L\left(T_0, p_0\right)\left[1 + \overline{\alpha} - \frac{1}{E}\left(1 - 2\nu\right)\left(p - p_0\right)\right]. \tag{2}$$

Therein, $\nu = 0.3$ is the Poisson number of the stainless steel 1.4571, which was provided by its supplier (Thyssen-Krupp Materials International) and $\overline{\alpha}$ is its integral thermal expansion coefficient between the temperatures T_0 and T[29]

$$\overline{\alpha} = \left[n_0\left(T - T_0\right) + \frac{n_1}{2}\left(T^2 - T_0^2\right) + \frac{n_2}{3}\left(T^3 - T_0^3\right) + \frac{n_3}{4}\left(T^4 - T_0^4\right) + \frac{n_4}{5}\left(T^5 - T_0^5\right)\right], \tag{3}$$

where $n_0 = 4.7341 \cdot 10^{-6}$ K^{-1}, $n_1 = 7.1518 \cdot 10^{-8}$ K^{-2}, $n_2 = -1.5273 \cdot 10^{-10}$ K^{-3}, $n_3 = 1.5864 \cdot 10^{-13}$ K^{-4} and $n_4 = -6.1342 \cdot 10^{-17}$ K^{-5}. Since the modulus of elasticity E is also temperature dependent, it was determined with a first order polynomial[29]

$$E = a + bT, \tag{4}$$

where $a = 219711.07$ MPa^{-1} and $b = -79.8$ K^{-1} MPa^{-1}. A comparison of the present calibration measurements with the equation of state by Wagner and Pruß,[24] along with the experimental data by Lin and Trusler with an uncertainty of 0.04%,[25] Al Ghafri et al.[30] with an uncertainty of 0.03% and several other authors, is presented in Figure 3. It is evident

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that for the 300 K and 350 K isotherms, the present results are in very good agreement with the equation of state, also at elevated pressures. The deviation is almost within 0.02% for these two isotherms. The maximum deviation is -0.23% for the 500 K isotherm at 2.7 MPa. However, it should be noted that the data by Lin and Trusler[25] also have large deviations of up to -0.11% for the 450 K isotherm and the equation of state is about 0.2% uncertain in this region.
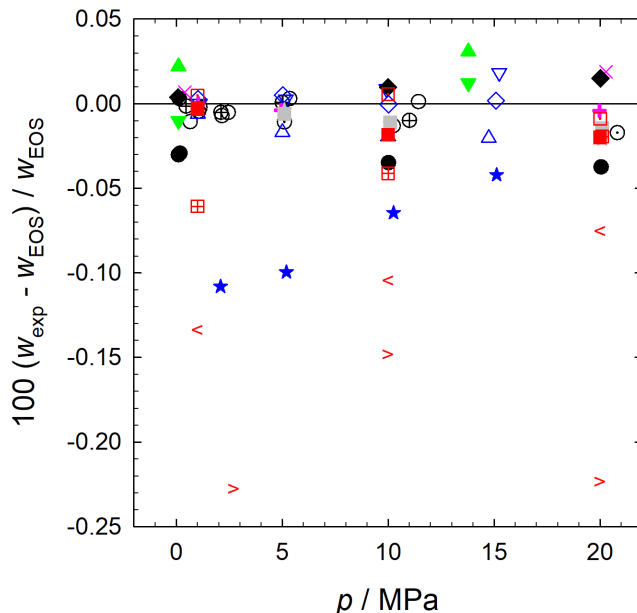

Figure 3: Comparison of the calibration measurements for the speed of sound of water with the equation of state by Wagner and Pruß.[24] Experimental data: this work, ■ 300 K, ⊡ 350 K, ⊞ 400 K, < 450 K, > 500 K; Javed et al.,[31] ⊙ 298 K, ⊕ 323 K, ◯ 361 K; Lin and Trusler,[25] △ 303 K, ◇ 323 K, ▽ 373 K ★ 453 K; Al Ghafri et al.,[30] + 306 K, × 358 K; Wilson,[32] ▲ 303 K, ▼ 364 K; Yebra et al.,[33] ■ 303 K, ★ 323 K; Benedetto et al.,[34] ● 303 K, ◆ 364 K.

Results and discussion

The speed of sound of diethylene glycol and triethylene glycol was measured in the liquid state along five isotherms, i.e. 300 K to 500 K in increments of 50 K. The pressure was varied from 0.1 MPa to 45 MPa. Since no accurate Helmholtz energy equations of state were

available, a double polynomial expression suggested by Sun et al.[5] and later implemented by several other authors[4,25,35] was fitted to the measured data of these glycols

$$(p - p_0)/\text{MPa} = \sum_{i=1}^{3} \sum_{j=0}^{2} a_{ij}[(w - w_0)/(\text{m s}^{-1})]^i (T/\text{K})^j. \tag{5}$$

Therein, the initial pressure is $p_0 = 0.1$ MPa and w_0 is the speed of sound at p_0. The temperature dependence of w_0 was fitted with a polynomial

$$w_0/(\text{m s}^{-1}) = \sum_{j=0}^{4} b_j (T/\text{K})^j, \tag{6}$$

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

$$\text{AAD} = \frac{100}{n} \sum_{i=1}^{n} \left| \frac{w_{\text{data}} - w_{\text{equation}}}{w_{\text{data}}} \right|_i, \tag{7}$$

where n is the number of experimental data points.

To correlate the present experimental data, equation (6) was fitted first to speed of sound data at p_0 to obtain the coefficients b_j. Equation (5) was subsequently fitted to all speed of sound data by minimizing the quadratic sum of the difference between the calculated and experimental speed of sound. For the 450 K and 500 K isotherms, it was not possible to measure w_0 because diethylene glycol is gaseous at 0.1 MPa. To estimate w_0 for these isotherms, equation (5) was fitted to the 450 K and 500 K isotherms individually. Subsequently, equation (6) was fitted to these calculated values for w_0 in an iterative way. The coefficients of equations (5) and (6) are listed in Table 5. Equation (5) has an average relative deviation of 0.043% for diethylene glycol and 0.008% for triethylene glycol.

The overall expanded uncertainty of the speed of sound at a confidence level of 95% ($k = 2$) includes the uncertainties of temperature u_T, pressure u_p, delay in time of flight $u_{\Delta t}$ and path length difference $u_{\Delta L}$.[4] The overall expanded uncertainty of the speed sound was

determined with the error propagation law

$$
\begin{aligned}
U_w \;=\; & k\Bigg[\left(\frac{\partial w}{\partial T}\right)^2_{p,\Delta L,\Delta t} u_T^2 + \left(\frac{\partial w}{\partial p}\right)^2_{T,\Delta L,\Delta t} u_p^2 \\
& + \left(\frac{\partial w}{\partial \Delta L}\right)^2_{T,p,\Delta t} u_{\Delta L}^2 + \left(\frac{\partial w}{\partial \Delta t}\right)^2_{T,p,\Delta L} u_{\Delta t}^2 \Bigg]^{1/2}.
\end{aligned}
\tag{8}
$$

The partial derivatives of the speed of sound with respect to temperature and pressure were calculated with equation (5), while the derivatives with respect to delay in time of flight and path length difference were determined from equation (1).

A detailed uncertainty budget for diethylene glycol and triethylene glycol is provided in Table 4. 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 uncertainty of the 25 Ω thermometer was assumed to be ten times larger than the value provided by the manufacturer because it was not in direct contact with the fluid. To reduce the pressure uncertainty, two transducers (type: Keller-PAA-33X) were used, having different operating ranges.The presence of pressure causes an elastic deformation of the silicon diaphragm of the integrated sensor chip. When auxiliary electrical energy was supplied, this deformation was converted proportionally into an electric signal, which was subsequently evaluated.

Table 4: Detailed uncertainty budget for the speed of sound of diethylene glycol and triethylene glycol.

source	type	measuring range	standard uncertainty	diethylene glycol[a]	triethylene glycol[a]
temperature	PT-25	84 - 693 K	0.02 K	0.041%	0.043%
pressure	Keller-PAA-33X	<10 MPa	0.002 MPa	0.007%	0.006%
	Keller-PAA-33X	<100 MPa	0.02 MPa		
time	oscilloscope	—	0.002 μs	0.031%	0.031%
path length	—	—	7 μm	0.071%	0.071%

[a] Relative expanded uncertainty ($k = 2$) value at a typical state point $T = 350$ K and $p = 20$ MPa.

Table 5: Coefficients of equations (5) and (6).

	diethylene glycol	triethylene glycol
a_{10}	$4.6799225 \cdot 10^{-01}$	$5.4669331 \cdot 10^{-01}$
a_{11}	$-5.8475137 \cdot 10^{-04}$	$-7.6345859 \cdot 10^{-04}$
a_{12}	$-1.6073934 \cdot 10^{-15}$	$4.5777364 \cdot 10^{-14}$
a_{20}	$5.3430583 \cdot 10^{-03}$	$1.7703447 \cdot 10^{-03}$
a_{21}	$-2.0880692 \cdot 10^{-05}$	$-7.7945805 \cdot 10^{-06}$
a_{22}	$2.0907681 \cdot 10^{-08}$	$9.2428456 \cdot 10^{-09}$
a_{30}	$-3.4460086 \cdot 10^{-05}$	$-5.3904122 \cdot 10^{-06}$
a_{31}	$1.4823129 \cdot 10^{-07}$	$2.7829901 \cdot 10^{-08}$
a_{32}	$-1.5815498 \cdot 10^{-10}$	$-3.4068752 \cdot 10^{-11}$
b_0	$4.5962805 \cdot 10^{+03}$	$3.0358819 \cdot 10^{+03}$
b_1	$-2.7226414 \cdot 10^{+01}$	$-8.2671241 \cdot 10^{+00}$
b_2	$9.8538175 \cdot 10^{-02}$	$1.9049639 \cdot 10^{-02}$
b_3	$-1.6901320 \cdot 10^{-04}$	$-2.9822883 \cdot 10^{-05}$
b_4	$1.0483863 \cdot 10^{-07}$	$1.7304190 \cdot 10^{-08}$

Speed of sound of diethylene glycol

The speed of sound data of diethylene glycol with experimental uncertainties at a confidence level of 95% ($k = 2$) are listed in Table 6. The speed of sound as a function of temperature and pressure in the liquid state covers a wide range between 1048.5 m s^{-1} to 1710.2 m s^{-1} and is depicted in Figure 4a. It can be seen that the speed of sound increases with pressure along isotherms because the liquid is compressed. Contrarily, the speed of sound decreases with rising temperature along isobars because the liquid expands.

Table 6: Speed of sound of liquid diethylene glycol with its expanded experimental uncertainty ($k = 2$) as a function of temperature T and pressure p,[1] measured with a frequency of 8 MHz.

T/K	p/MPa	w/(m s^{-1})	U_w/(m s^{-1})	T/K	p/MPa	w/(m s^{-1})	U_w/(m s^{-1})
300.10	0.10	1582.4	1.2	400.00	10.00	1377.6	1.1
300.04	1.00	1585.0	1.2	400.00	20.00	1414.7	1.3
300.00	2.00	1588.2	1.2	400.00	30.00	1449.7	1.3
299.99	5.00	1597.4	1.3	400.00	40.00	1482.8	1.3

Table 6 : (Continued)

T/K	p/MPa	w/(m s^{-1})	U_w/(m s^{-1})	T/K	p/MPa	w/(m s^{-1})	U_w/(m s^{-1})
300.00	10.00	1612.3	1.3	400.00	45.00	1498.8	1.3
300.01	20.00	1640.9	1.3	450.00	0.22	1196.7	0.9
299.99	30.01	1670.0	1.4	450.00	1.00	1200.5	0.9
300.01	40.00	1696.9	1.5	450.00	2.00	1205.3	0.9
300.01	45.00	1710.2	1.5	450.00	5.00	1219.2	0.9
350.05	0.10	1464.7	1.1	450.00	10.00	1241.8	1.0
350.03	1.00	1468.3	1.1	450.00	20.01	1284.8	1.3
350.00	2.00	1472.0	1.1	450.00	30.01	1324.8	1.3
350.14	5.01	1483.8	1.1	450.00	40.01	1362.4	1.2
350.00	10.00	1503.2	1.2	450.00	45.00	1380.3	1.3
350.02	20.00	1534.5	1.3	500.00	1.00	1048.5	0.8
350.01	29.92	1565.5	1.4	499.99	2.00	1054.1	0.8
350.06	40.01	1596.2	1.4	500.00	5.00	1070.8	0.8
350.00	45.00	1613.3	1.4	500.00	10.00	1098.1	0.8
400.00	0.10	1338.9	1.0	500.00	20.00	1148.6	1.3
400.00	0.99	1342.5	1.0	500.01	30.00	1195.0	1.3
400.00	2.01	1346.5	1.0	499.91	40.00	1237.9	1.3
400.00	5.00	1358.3	1.0	499.97	45.00	1258.1	1.2

[1] U_w is the expanded uncertainty of speed of sound at a confidence level of 95% ($k = 2$), composed of standard uncertainties of temperature $u_T = 0.02$ K, pressure $u_p = 0.02$ MPa, delay in time of flight $u_{\Delta t} = 0.002$ μs and path length difference $u_{\Delta L} = 7$ μm.

A graphical representation of the experimental uncertainty of the speed of sound as a function of pressure along different isotherms is provided in Figure 4b. The expanded uncertainty of the entire data set is below 0.11%. It should be noted that the data have

uncertainties below 0.08% for a pressure up to 10 MPa because the pressure was measured with a more accurate transducer, cf. Table 4. This transducer had a standard uncertainty of 0.002 MPa in terms of pressure, while the second transducer with a pressure range of up to 100 MPa had a standard uncertainty of 0.02 MPa. Consequently, the relative expanded uncertainty in the speed of sound data is larger at pressures above 10 MPa.
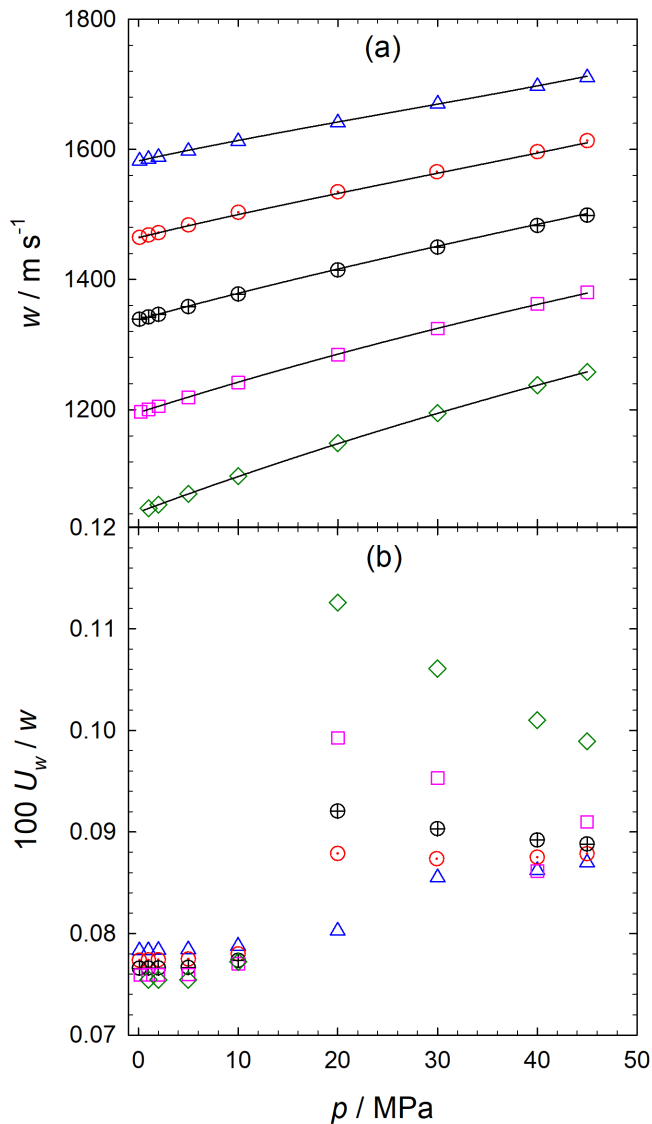

Figure 4: Speed of sound of diethylene glycol (a) and its experimental uncertainty (b) as a function of pressure along isotherms: △ 300 K, ⊙ 350 K, ⊕ 400 K, □ 450 K, ◇ 500 K.

Relative deviations of the present speed of sound data of diethylene glycol from equation

(5) are shown in Figure 5. All isotherms are provided individually, where the error bars represent the relative expanded uncertainty. It can be seen that the correlatoin is in very good agreement with the measured data along the 300 K, 450 K and 500 K isotherms, having a maximum deviation of about 0.1%. For the 350 K and 400 K isotherms, the deviations are larger at some state points with a maximum of about 0.2%. However, it should be noted that the experimental uncertainties of the present data are between 0.08% and 0.11%.
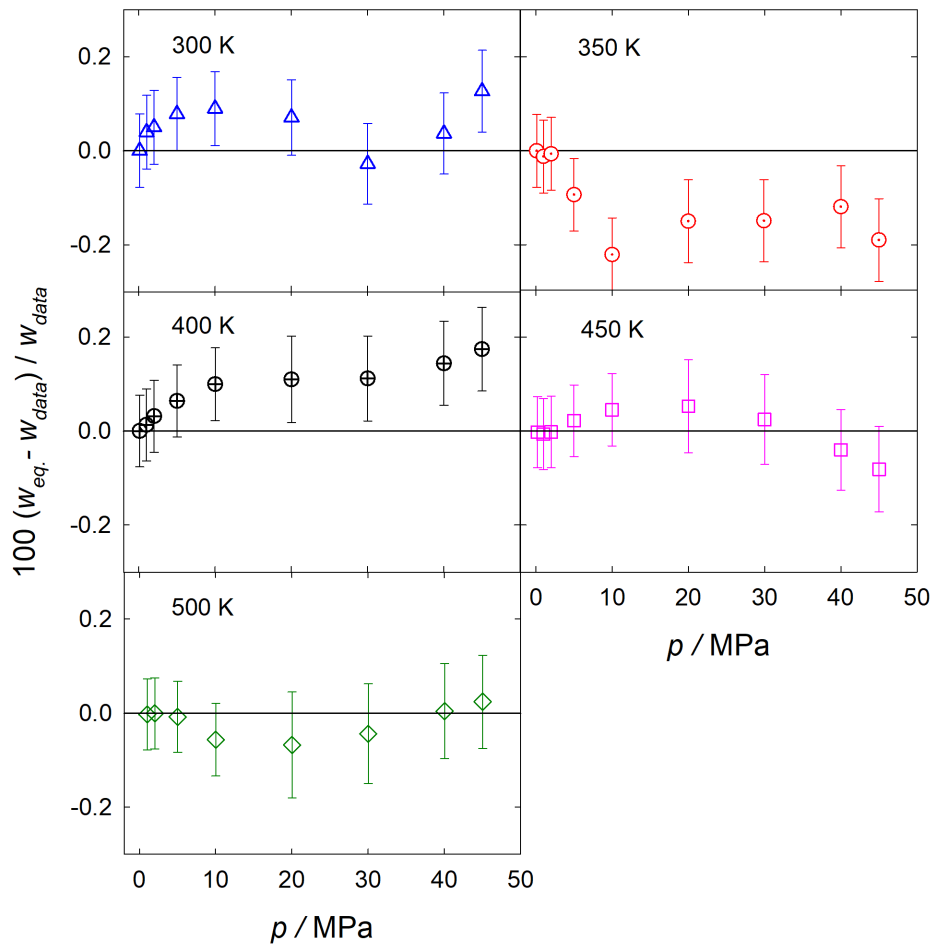

Figure 5: Deviation of speed of sound of diethylene glycol from equation (5).

A comprehensive comparison of the present speed of sound data with literature values and equation (5) is presented in Figure 6. A total of 15 authors have reported the speed of

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sound of diethylene glycol at 66 state points, covering the temperature range between 273 K and 473 K. However, all authors have measured the speed of sound below 0.4 MPa. Thereof, six authors have provided the speed of sound at a single state point.

The comparison shows that literature data deviate by up to 2% from the present data and equation (5). Zotov and Shoitov[10] as well as George and Sastry[13] reported 19 and six state points, respectively. The present measurements confirm their data near ambient temperature, but the deviations are large at elevated temperatures. Willard[7] as well as Kishimoto and Nomoto[6] presented data points at ambient conditions that are also in very good agreement with the present results with a deviation of about 0.07%. Other data usually deviate between 0.4% and 1%.
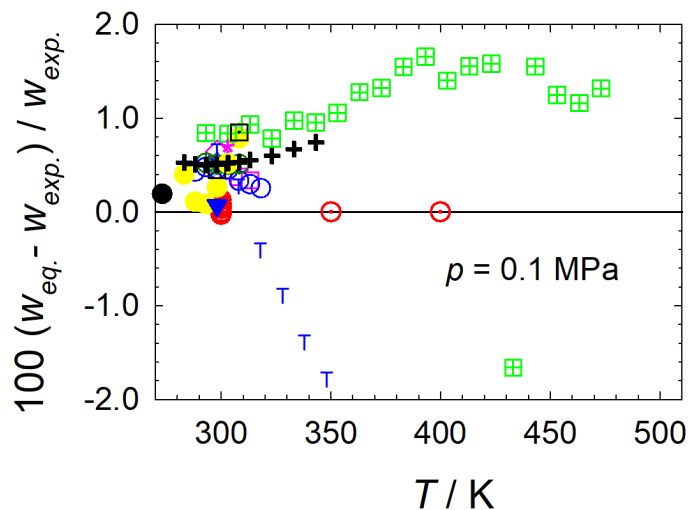

Figure 6: Deviation of speed of sound data for diethylene glycol from equation (5). Experimental data: this work ⊙, Zotov and Shoitov[10] ⊞, Willard[7] ▼, Kishimoto and Nomoto[6] •, Marks[9] ●, Aminabhavi and Gopalakrishna[11] ◇, Sastry and Patel[12] ⊡, George and Sastry[13] ⊤, Mehta et al.[14] *, Sastry et al.[8] ★, Ćwiklińska et al.[15] △, Tsierkezos and Palaiologou[16] ×, Carvalho et al.[17] +, Ali et al.[18] □, Klimaszewski et al.[19] ◯, Hoga et al.[20] ⊕.

Speed of sound of triethylene glycol

The speed of sound of triethylene glycol with experimental uncertainties at a confidence level of 95% ($k = 2$) are listed in Table 7. The speed of sound as a function of temperature and pressure in the liquid state covers a wide range between 1018.4 m s^{-1} to 1733.6 m s^{-1} and is presented in Figure 7a.
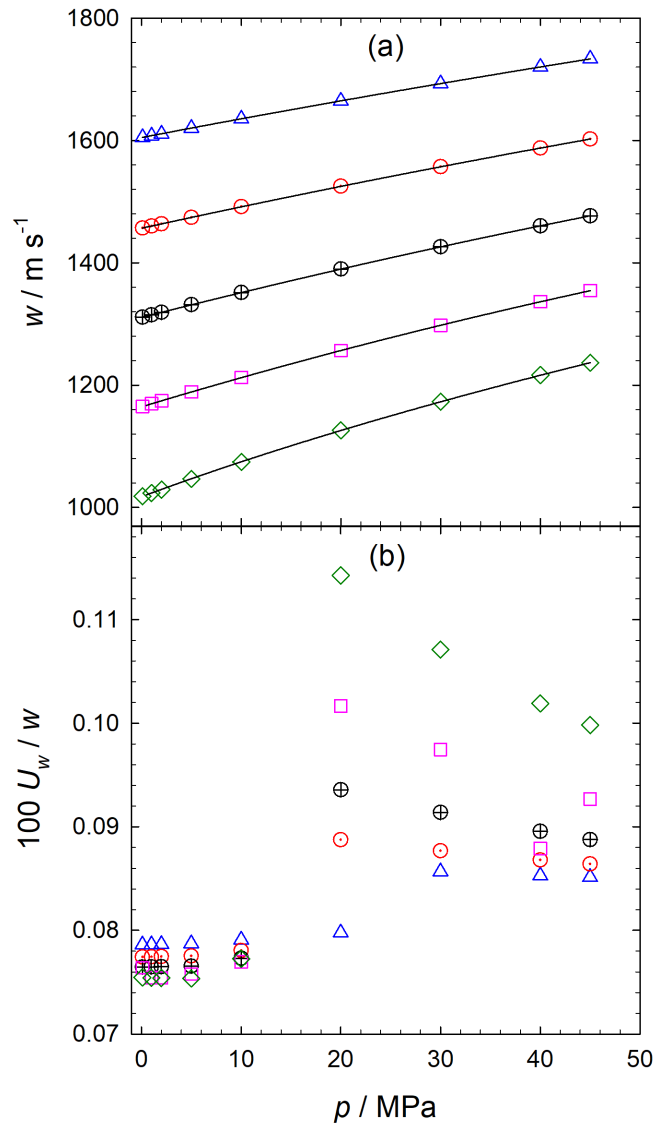

Figure 7: Speed of sound of triethylene glycol (a) and its experimental uncertainty (b) as a function of pressure along isotherms: △ 300 K, ⊙ 350 K, ⊕ 400 K, □ 450 K, ◇ 500 K.

A graphical representation of the experimental uncertainty of the speed of sound as a

function of pressure along different isotherms is provided in Figure 7b. The experimental uncertainties vary between 0.07% to 0.012%. The largest contribution to the overall uncertainty is due to path length calibration, i.e. 0.07%, which also includes the uncertainty of the equation of state and the deviation of the present data from the equation of state at elevated temperature and pressure. The uncertainties are large at pressures above 10 MPa because the pressure was measured with a less accurate transducer, as explained above.

Table 7: Speed of sound of liquid triethylene glycol with its expanded experimental uncertainty ($k = 2$) as a function of temperature T and pressure p,[1] measured with a frequency of 8 MHz.

T/K	p/MPa	w/(m s^{-1})	U_w/(m s^{-1})	T/K	p/MPa	w/(m s^{-1})	U_w/(m s^{-1})
300.00	0.10	1605.2	1.3	400.00	20.00	1389.9	1.3
300.00	1.00	1607.9	1.3	400.00	30.01	1426.2	1.3
300.00	2.00	1610.9	1.3	400.00	40.00	1460.5	1.3
300.00	5.00	1620.2	1.3	400.00	45.00	1476.9	1.3
300.00	10.00	1635.3	1.3	450.00	0.10	1165.2	0.9
300.00	20.00	1664.8	1.3	450.00	1.00	1169.7	0.9
300.00	30.00	1693.0	1.5	450.00	2.00	1174.6	0.9
300.00	40.00	1720.2	1.5	450.00	5.00	1189.1	0.9
300.00	45.00	1733.6	1.5	450.00	10.00	1212.6	0.9
350.00	0.10	1457.0	1.1	450.00	20.00	1256.7	1.3
350.00	1.00	1460.2	1.1	450.00	30.00	1297.8	1.3
350.00	2.00	1463.7	1.1	450.00	40.00	1336.5	1.2
350.00	5.00	1474.4	1.1	450.00	45.00	1354.8	1.3
350.00	10.00	1491.8	1.2	500.00	0.10	1018.4	0.8
350.00	20.00	1525.4	1.4	499.99	1.00	1023.8	0.8
350.00	30.00	1557.2	1.4	500.00	2.00	1029.5	0.8
350.00	40.00	1587.6	1.4	500.00	5.00	1046.9	0.8

Table 7 : (Continued)

T/K	p/MPa	$w/(\text{m s}^{-1})$	$U_w/(\text{m s}^{-1})$	T/K	p/MPa	$w/(\text{m s}^{-1})$	$U_w/(\text{m s}^{-1})$
350.00	45.00	1602.5	1.4	500.00	10.00	1074.6	0.8
400.00	0.10	1311.3	1.0	500.00	20.00	1126.0	1.3
400.00	1.00	1314.9	1.0	500.00	30.00	1173.0	1.3
400.00	2.00	1319.2	1.0	499.98	40.00	1216.5	1.2
400.00	5.00	1331.5	1.0	500.00	45.00	1236.8	1.2
400.00	10.00	1351.6	1.0				

[1] U_w is the expanded uncertainty of speed of sound at a confidence level of 95% ($k = 2$), composed of standard uncertainties of temperature $u_T = 0.02$ K, pressure $u_p = 0.02$ MPa, delay in time of flight $u_{\Delta t} = 0.002$ μs and path length difference $u_{\Delta L} = 7$ μm.

Relative deviations of the present speed of sound data of triethylene glycol from equation (5) are shown in Figure 8. All isotherms are provided individually, where the error bars represent the relative expanded uncertainty. It can be seen that equation (5) was fitted with a maximum deviation of 0.04% only, which is four times better than the equation for diethylene glycol. The main reason is that for triethylene glycol, it was possible to measure the speed of sound w_0 at 0.1 MPa up to 500 K, which was necessary for fitting equation (6), while diethylene glycol is gaseous above 430 K.

A comprehensive comparison of the present speed of sound data with literature values and equation (5) is presented in Figure 9. A total of 12 authors have reported the speed of sound of triethylene glycol at 48 state points, covering the temperature range between 273 K and 348 K. However, similar to diethylene glycol, all authors have measured the speed of sound at ambient pressure only, while six authors have provided a single data point. Comparison shows that literature data exhibit deviations of up to about 3% from the present data and from equation (5). Kishimoto and Nomoto,[6] Carvalho et al.[17] and Klimaszewski et al.[21] have reported five, 10 and 14 state points, respectively. It is evident that their data confirm
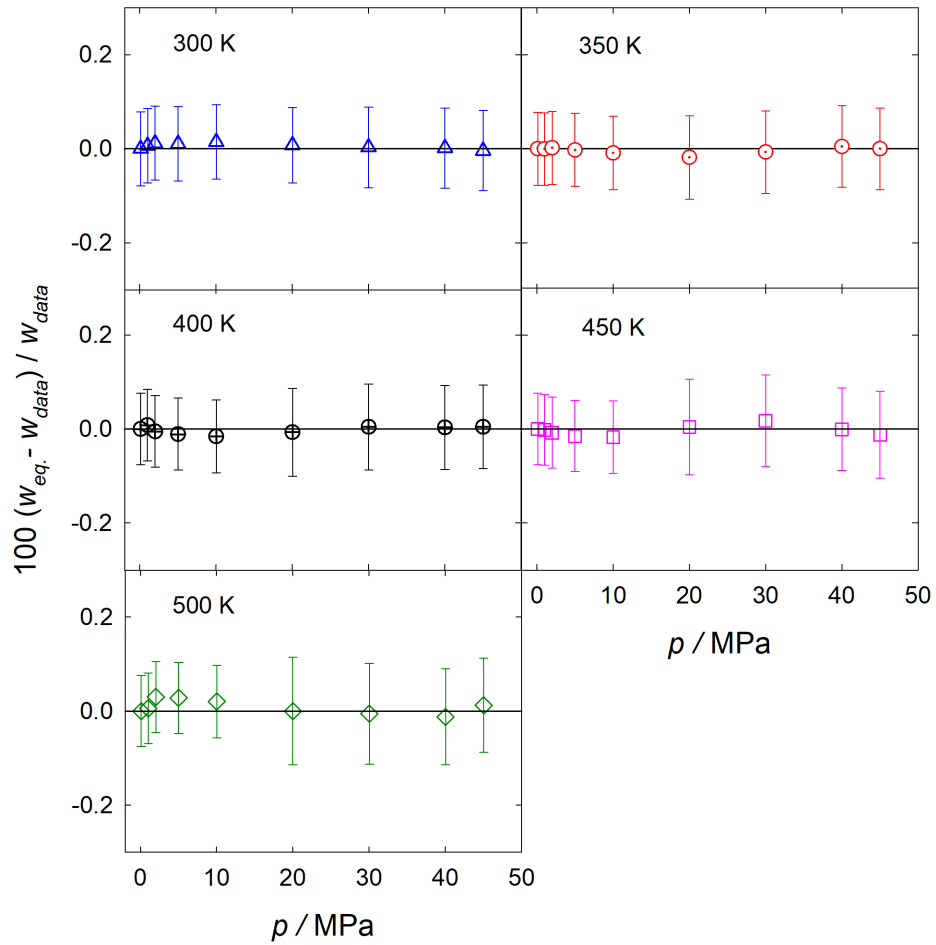
Figure 8: Deviation of speed of sound of triethylene glycol from equation (5).

the present measurements at some state points, but systematically deviate from the present data at higher or lower temperatures. Sastry and Patel[12] published the speed of sound of triethylene glycol at two state points. Their point at ambient conditions is in very good agreement with the present work, having a deviation of 0.08%. However, the data by George and Sastry[13] have a deviation of up to 3% from the present work and from equation (5).
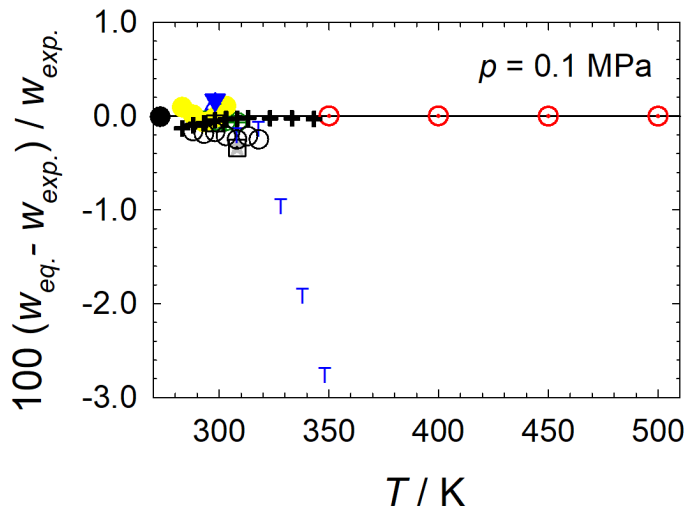

Figure 9: Deviation of speed of sound of triethylene glycol from equation (5). Experimental data: this work ⊙, Willard[7] ▼, Kishimoto and Nomoto[6] ●, Marks[9] ●, Sastry and Patel[12] ⊡, George and Sastry[13] ⊤, Mehta et al.[14] *, Sastry et al.[8] ★, Ćwiklińska et al.[15] △, Tsierkezos and Palaiologou[16] ×, Carvalho et al.[17] +, Hoga et al.[20] ⊕, Klimaszewski et al.[21] ◯.

Conclusions

In a certain frequency range, the speed of sound is a thermodynamic property, characterizing the interplay of pressure and density at constant entropy, thus having a thermal and caloric nature. Such data are important for the development of highly accurate Helmholtz energy equations of state, which allow for the calculation of all thermodynamic properties. Therefore, equations of state of this type are needed in numerous chemical and process industries to optimize their operations. In the present work, an apparatus based on the pulse-echo tech-

nique was designed and built to measure the thermodynamic speed of sound of diethylene glycol and triethylene glycol. The path length of its acoustic cell was calibrated with distilled water of $\geqslant 99.99\%$ purity on the basis of a reference quality Helmholtz energy equation of state by Wagner and Pruß.[24] The calibration measurements were also compared with very accurate experimental literature data. Subsequently, diethylene glycol and triethylene glycol were sampled with the apparatus for measuring the speed of sound, covering the temperature range between 300 K and 500 K and a pressure of up to 45 MPa. A detailed experimental uncertainty analysis was carried out with the error propagation law and a coverage factor $k = 2$. It was found that the data have a maximum expanded uncertainty of 0.11% for the glycols.

Because no accurate equations of state were available for these glycols, a double-polynomial equation was fitted to the present data with an average relative deviation of 0.043% for diethylene glycol and 0.008% for triethylene glycol. A comparison of the present data with these correlations and literature data was made. For both glycols, literature data were available almost only at the ambient pressure. Near ambient temperature, literature data are in good agreement with the present data. However, the deviations are significant at high temperatures, having a maximum value of 2% for diethylene glycol and 3% for triethylene glycol.

Acknowledgements

References

(1) Rebsdat, S.; Mayer, D. Ethylene Glycol. *Ullmann's Encycl. Ind. Chem.* **2000**, *495*.

(2) Thol, M.; Javed, M. A.; Baumhögger, E.; Span, R.; Vrabec, J. Thermodynamic Properties of Dodecamethylpentasiloxane, Tetradecamethylhexasiloxane, and Decamethyl-cyclopentasiloxane. *Ind. Eng. Chem. Res.* **2019**, *58*, 9617–9635.

(3) Javed, M. A.; Baumhögger, E.; Vrabec, J. Thermodynamic Speed of Sound of Xenon. *J. Chem. Thermodyn.* **2020**, *141*, 105933.

(4) Javed, M. A.; Baumhögger, E.; Vrabec, J. Thermodynamic Speed of Sound Data for Liquid and Supercritical Alcohols. *J. Chem. Eng. Data* **2019**, *64*, 1035–1044.

(5) Sun, T. F.; Schouten, J. A.; Biswas, S. N. Determination of the Thermodynamic Properties of Liquid Ethanol from 193 to 263 K and up to 280 MPa from Speed-of-Sound Measurements. *Int. J. Thermophys.* **1991**, *12*, 381–395.

(6) Kishimoto, T.; Nomoto, O. Absorption of Ultrasonic Waves in Organic Liquids (II) Liquids with Negative Temperature Coefficient of Sound Absorption (a) Glycols, Cyclohexanol and Cresol. *J. Phys. Soc. Jpn.* **1954**, *9*, 1021–1029.

(7) Willard, G. Temperature Coefficient of Ultrasonic Velocity in Solutions. *J. Acoust. Soc. Am.* **1947**, *19*, 235–241.

(8) Sastry, N. V.; Thakor, R. R.; Patel, M. C. Thermophysical Properties for Diethylene Glycol+ Nitrobenzene and Triethylene Glycol+(Chloro-, Bromo-, Nitro-) Benzene Systems at Different Temperatures. *Int. J. Thermophys.* **2008**, *29*, 610–618.

(9) Marks, G. W. Acoustic Velocity with Relation to Chemical Constitution in Alcohols. *J. Acoust. Soc. Am.* **1967**, *41*, 103–117.

(10) Zotov, V. V.; Shoitov, Y. S. Ultrasound and Physico Chemical Properties of Substances [in Russian]. *Kursk Pedagogical Institute, Kursk* **1970**, *71*, 92–97.

(11) Aminabhavi, T. M.; Gopalakrishna, B. Density, Viscosity, Refractive Index, and Speed of Sound in Aqueous Mixtures of N, N-Dimethylformamide, Dimethyl Sulfoxide, N,

N-Dimethylacetamide, Acetonitrile, Ethylene Glycol, Diethylene Glycol, 1, 4-Dioxane, Tetrahydrofuran, 2-Methoxyethanol, and 2-Ethoxyethanol at 298.15 K. *J. Chem. Eng. Data* **1995**, *40*, 856–861.

(12) Sastry, N. V.; Patel, M. C. Densities, Excess Molar Volumes, Viscosities, Speeds of Sound, Excess Isentropic Compressibilities, and Relative Permittivities for Alkyl (Methyl, Ethyl, Butyl, and Isoamyl) Acetates+ Glycols at Different Temperatures. *J. Chem. Eng. Data* **2003**, *48*, 1019–1027.

(13) George, J.; Sastry, N. Partial Excess Molar Volumes, Partial Excess Isentropic Compressibilities and Relative Permittivities of Water+ Ethane-1, 2-Diol Derivative and Water+ 1, 2-Dimethoxyethane at Different Temperatures. *Fluid Phase Equilib.* **2004**, *216*, 307–321.

(14) Mehta, S.; Ram, G.; Sharma, A. Effect of Oxyethylene Groups on the Behaviour of Thermodynamic Properties of Pyrrolidin-2-one and Poly (Ethylene Glycols). *Fluid Phase Equilib.* **2004**, *220*, 153–160.

(15) Ćwiklińska, A.; Miecznik, P.; Klimczak, M.; Kinart, C. M. Viscosimetric and Ultrasonic Studies of Intermolecular Interactions of 2-Methoxyethanol with Diethylene Glycol, Triethylene Glycol and Tetraethylene Glycol Binary Mixtures. *Phys. Chem. Liq.* **2008**, *46*, 454–463.

(16) Tsierkezos, N. G.; Palaiologou, M. M. Ultrasonic Studies of Liquid Mixtures of Either Water or Dimethylsulfoxide with Ethylene Glycol, Diethylene Glycol, Triethylene Glycol, Tetraethylene Glycol, 1, 2-Propylene Glycol and 1, 4-Butylene Glycol at 298.15 K. *Phys. Chem. Liq.* **2009**, *47*, 447–459.

(17) Carvalho, P. J.; Fonseca, C. H.; Moita, M.-L. C.; Santos, A. F.; Coutinho, J. A. Thermophysical Properties of Glycols and Glymes. *J. Chem. Eng. Data* **2015**, *60*, 3721–3737.

(18) Ali, A.; Ansari, S.; Uzair, S.; Tasneem, S.; Nabi, F. Densities, Ultrasonic Speeds, and Excess Properties of Binary Mixtures of Diethylene Glycol with 1-Butanol, 2-Butanol, and 1, 4-Butanediol at Different Temperatures. *Int. J. Thermophys.* **2015**, *36*, 3153–3168.

(19) Klimaszewski, K.; Stronka-Lewkowska, E.; Soliwoda, K.; Bald, A. Acoustic and Volumetric Studies on Water+ Diethylene Glycol Mixtures in a Wide Temperature Range. Comparison with Mixtures of Water with Tri- and Tetraethylene Glycol. *J. Mol. Liq.* **2016**, *215*, 520–533.

(20) Hoga, H. E.; Torres, R. B.; Volpe, P. L. O. Thermodynamics Properties of Binary Mixtures of Aqueous Solutions of Glycols at Several Temperatures and Atmospheric Pressure. *J. Chem. Thermodyn.* **2018**, *122*, 38–64.

(21) Klimaszewski, K.; Stronka-Lewkowska, E.; Abramczyk, K.; Bald, A. Acoustic and volumetric studies on (triethylene glycol+ water) mixtures in a wide temperature range. *J. Chem. Thermodyn.* **2015**, *89*, 212–222.

(22) Ball, S.; Trusler, J. Speed of Sound of n-Hexane and n-Hexadecane at Temperatures Between 298 and 373 K and Pressures up to 100 MPa. *Int. J. Thermophys.* **2001**, *22*, 427–443.

(23) Meier, K.; Kabelac, S. Speed of Sound Instrument for Fluids with Pressures up to 100 MPa. *Rev. Sci. Instrum.* **2006**, *77*, 123903.

(24) Wagner, W.; Pruß, A. The IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use. *J. Phys. Chem. Ref. Data* **2002**, *31*, 387–535.

(25) Lin, C. W.; Trusler, J. P. The Speed of Sound and Derived Thermodynamic Properties of Pure Water at Temperatures between (253 and 473) K and at Pressures up to 400 MPa. *J. Chem. Phys.* **2012**, *136*, 094511.

(26) Marczak, W. Water as a Standard in the Measurements of Speed of Sound in Liquids. *J. Acoust. Soc. Am.* **1997**, *102*, 2776–2779.

(27) Del Grosso, V. A.; Mader, C. W. Speed of Sound in Pure Water. *J. Acoust. Soc. Am.* **1972**, *52*, 1442–1446.

(28) Fujii, K.; Masui, R. Accurate Measurements of the Sound Velocity in Pure Water by Combining a Coherent Phase-Detection Technique and a Variable Path-Length Interferometer. *J. Acoust. Soc. Am.* **1993**, *93*, 276–282.

(29) Gedanitz, H.; Dávila, M. J.; Baumhögger, E.; Span, R. An Apparatus for the Determination of Speeds of Sound in Fluids. *J. Chem. Thermodyn.* **2010**, *42*, 478–483.

(30) Al Ghafri, S. Z.; Matabishi, E. A.; Trusler, J. M.; May, E. F.; Stanwix, P. L. Speed of Sound and Derived Thermodynamic properties of para-Xylene at Temperatures between (306 and 448) K and at Pressures up to 66 MPa. *J. Chem. Thermodyn.* **2019**, *135*, 369–381.

(31) Javed, M. A.; Rüther, M.; Baumhögger, E.; Vrabec, J. Density and Thermodynamic Speed of Sound of Liquid Vinyl Chloride. *J. Chem. Eng. Data* **2020**, *65*, 2495–2504.

(32) Wilson, W. D. Speed of Sound in Distilled Water as a Function of Temperature and Pressure. *J. Acoust. Soc. Am.* **1959**, *31*, 1067–1072.

(33) Yebra, F.; Troncoso, J.; Romaní, L. Fully Automatized Apparatus for Determining Speed of Sound for Liquids in the Temperature and Pressure Interval (283.15–343.15) K and (0.1–95) MPa. *J. Chem. Thermodyn.* **2017**, *104*, 102–109.

(34) Benedetto, G.; Gavioso, R.; Albo, P. G.; Lago, S.; Ripa, D. M.; Spagnolo, R. Speed of Sound in Pure Water at Temperatures between 274 and 394 K and at Pressures up to 90 MPa. *Int. J. Thermophys.* **2005**, *26*, 1667–1680.

(35) Javed, M. A. Speed of Sound Measurement for Industrially Important Fluids with the
Pulse-Echo Technique. Doctoral Thesis, Technische Universität Berlin, Berlin, 2020.

Supporting Information:

Apparatus for the measurement of the thermodynamic speed of sound of diethylene glycol and triethylene glycol

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Calibration measurements

Table 1: Speed of sound of liquid water with its expanded experimental uncertainty ($k = 2$) as a function of varying temperature T and pressure p,[1] measured with a frequency of 8 MHz.

T/K	p/MPa	w/(m s^{-1})	U_w/(m s^{-1})	T/K	p/MPa	w/(m s^{-1})	U_w/(m s^{-1})
300.03	1.000	1503.1	1.2	400.01	20.097	1555.6	1.2

Table 1 : (Continued)

T/K	p/MPa	$w/(\mathrm{m\ s^{-1}})$	$U_w/(\mathrm{m\ s^{-1}})$	T/K	p/MPa	$w/(\mathrm{m\ s^{-1}})$	$U_w/(\mathrm{m\ s^{-1}})$
300.03	10.001	1518.0	1.2	450.08	0.994	1398.5	1.1
300.02	20.001	1534.7	1.2	450.00	10.000	1426.9	1.1
350.01	1.001	1556.8	1.2	449.99	19.997	1456.6	1.1
350.00	10.001	1574.3	1.2	500.00	2.714	1237.1	0.9
349.99	20.003	1593.1	1.2	500.01	9.998	1269.3	1.1
400.01	1.002	1510.3	1.2	500.01	20.000	1308.3	1.1
400.03	9.999	1532.0	1.2				

[1] U_w is the expanded uncertainty of speed of sound at a confidence level of 95% ($k = 2$), composed of standard uncertainties of temperature $u_T = 0.02$ K, pressure $u_p = 0.02$ MPa, delay in time of flight $u_{\Delta t} = 0.002$ μs and path length difference $u_{\Delta L} = 7$ μm.