Density and thermodynamic speed of sound of liquid vinyl chloride

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Abstract

Vinyl chloride is one of the world's most important industrially synthesized substances, but due to its physico-chemical nature comparably little is known about its thermodynamic behavior. Accurate density and thermodynamic speed of sound data of vinyl chloride in the liquid state are measured along nine isotherms, covering the temperature range from 283 K to 362 K up to a pressure of 91 MPa. Data are presented with a maximum expanded uncertainty ($k = 2$) of 0.15% for the density and 0.16% for the speed of sound. They are compared with all available literature sources and a preliminary equation of state. Present density data are in good agreement with the literature data and have a maximum deviation of 1.5% from the equation of state. However, no experimental speed of sound data are available in the literature for comparison and the equation of state diverges up to -12.4% from the present data.

keywords: Density, speed of sound, densimeter, pulse-echo technique, vinyl chloride.

1   Introduction

Vinyl chloride, a common name for chloroethene, chloroethylene, ethylene monochloride or monochloroethylene, is under ambient conditions a colorless and combustible gas with a mildly sweet odor. It is one of the world's most important industrial commodity chemicals, but it can also be formed in the environment, when chlorinated solvents are broken down by soil microorganisms.[1,2] Vinyl chloride is toxic for humans, since acute or short-term exposure during respiration damages the central nervous system, while long-term exposure results in liver cancer.[1,3]

The global production of vinyl chloride monomer was 49 million metric tons in 2018 and it is expected to reach 53 million metric tons by 2023.[4] Northeast Asia is currently the largest consumer of vinyl chloride, utilizing more than half of its total production. China is the biggest player in the vinyl chloride industry, consuming about 40% of its total yield, while the United States is in the second place.[5]

Vinyl chloride was commercially produced for the first time in the 1930s. Currently, it is synthesised by direct chlorination or oxychlorination of ethylene. As a result of both processes, 1,2-dichloroethane is obtained, which is subjected to a pressure of about 3 MPa at a temperature of 550 °C. This causes 1,2-dichloroethane to undergo pyrolysis or thermal cracking, forming vinyl chloride monomer and hydrogen chloride, from which vinyl chloride is isolated.[1,6]

Almost 99% of the total production of vinyl chloride is used for making polyvinyl chloride (PVC), which contains repeating units of vinyl chloride monomer in long chains. This polymer is commonly utilized with great flexibility to make end products, including pipes and fittings, profiles and tubes, siding, wire coating, housewares and automotive parts. The vinyl chain, containing ethylene dichloride, vinyl chloride monomer and polyvinyl chloride, is a main component of the petrochemical and thermoplastic industry.[5] Vinyl chloride is also used to produce methyl chloroform and copolymers with vinyl acetate, vinyl stearate and

vinylidene chloride.[1] In the past, vinyl chloride was used as a refrigerant, propellant in spray cans and in some cosmetics, but these practices have been officially banned since the 1970s.[1]

Because vinyl chloride has critical health and fire hazards and can easily undergo polymerization reactions,[15] very limited experimental data for the density and no data for the speed of sound have been reported in the literature, cf. Table 1. Eight authors have measured the density in the liquid phase, covering the temperature range from 213 K to 423 K up to a maximum pressure of 4.2 MPa, cf. Figure 1. However, most have measured only along the vapor pressure line. Cullick and Ely[12] as well as Zerfa and Brooks[14] have investigated higher pressures, but the latter have reported only a single data point.

Density and the speed of sound data, covering wide temperature and pressure ranges, are necessary for the development and parameterization of Helmholtz energy equations of state.[16] As the global demand for vinyl chloride is increasing rapidly,[5] a precise equation of state is beneficial for the design and optimization of industrial chemical processes. However, the currently available literature data for vinyl chloride are insufficient to properly parameterize such models. Nonetheless, a preliminary Helmholtz energy equation of state of Thol and Span[17] exists.

In the present work, an apparatus was built to simultaneously measure the density and speed of sound of vinyl chloride. To suppress the risk of polymerization, copper wires were avoided and hydroquinone was placed in the rig as a stabilizer.[18] The measurements were performed in the liquid phase, covering the temperature range from 283 K to 362 K up to a pressure of 91 MPa. The density was measured with an Anton Paar densimeter (DMA-HPM) with a maximum expanded uncertainty of 0.15% ($k = 2$). The speed of sound was investigated by employing a double path length pulse-echo technique with a maximum expanded uncertainty of 0.16% ($k = 2$). The obtained results were compared with the available literature data and the preliminary Helmholtz energy equation of state of Thol and Span.[17]

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2 Experiment

2.1 Materials

The specifications of the materials and details of their suppliers are provided in Table 2. They were purchased under high purity and studied without any further purification, except for degassing the liquid water sample.

2.2 Apparatus

An apparatus was developed to simultaneously sample the density and the speed of sound of vinyl chloride. For this purpose, a densimeter and an acoustic cell were combined. The schematic of the experimental rig is presented in Figure 2. To specify a temperature, both measurement devices were connected to a thermostat (Huber CC415). Therein, water was circulated as a heat transfer medium to regulate and maintain the temperature of the sample fluid within 0.01 K. The temperature was varied between 283 K and 362 K, remaining about 11 K below the normal boiling point of water to prevent excessive evaporation and to protect the circulating pump and electric circuits from damage caused by moisture. A hand pump (HIP 50-6-15) was employed to impose a pressure of up to 91 MPa that was measured by a pressure transducer (Keller-PAA-33X).

Vinyl chloride is a highly unstable monomer and undergoes rapid polymerization reactions to form polyvinyl chloride (PVC) by heating and under the influence of air, sunlight and contact with strong oxidizers and metals, i.e. copper and aluminum.[15] It is a gas under ambient conditions and its mixture with air forms peroxide, which may explode.[19] Moreover, in the presence of moisture, vinyl chloride reacts with iron or steel. To mitigate this risk, the copper quantity in the apparatus was reduced to a minimum level and crystalline hydroquinone was used to prevent spontaneous polymerization.[18] As this stabilizer is not soluble in vinyl chloride, almost 5 g of it was placed in a container with a porous lid behind
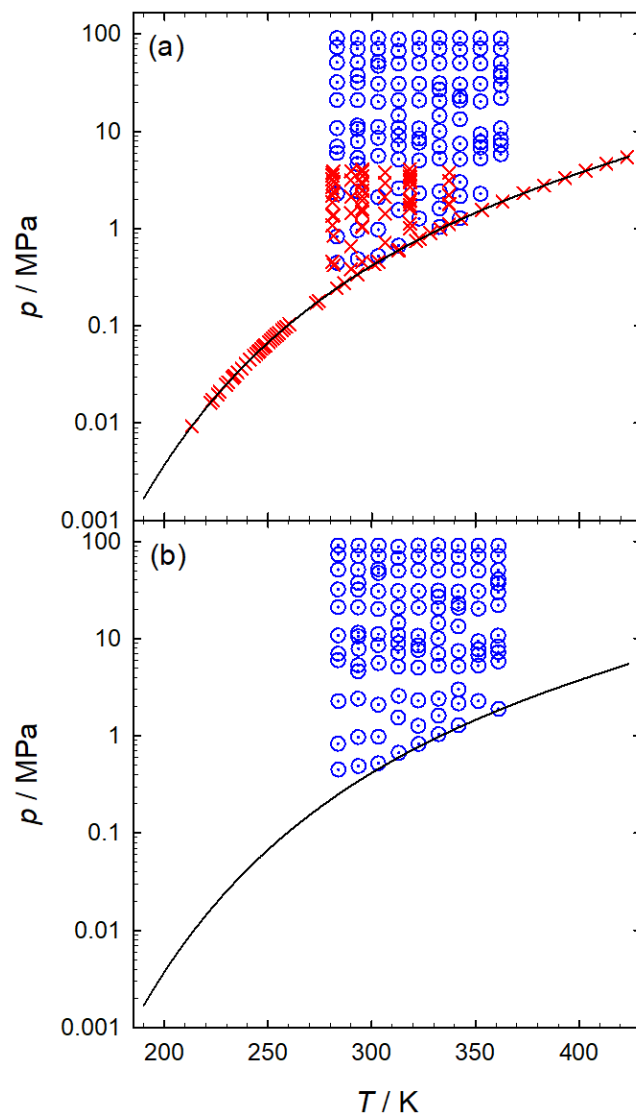
Figure 1: State points where (a) density and (b) speed of sound of vinyl chloride were measured: ⊙ this work, × experimental literature data. The solid line is the vapor pressure curve.

one of the reflectors, cf. Figure 3. The diameter of the lid pores was smaller than the crystal size of hydroquinone, keeping it in the container. The acoustic cell with the container was screwed into the ceiling of the pressure vessel. The cell was suspended in the sample fluid and to uniformly fill it, reflectors with cavity spacers were used.

2.3 Density measurement

The density of vinyl chloride was measured with an Anton Paar densimeter (DMA-HPM). Therein, a U-shaped metallic vibrating tube is connected to an interface module, which generates an oscillation and measures its period and temperature of the tube containing the sample fluid. The oscillation period is a function of density, temperature and pressure. To accurately determine the density of vinyl chloride, the densimeter was calibrated with propane and water on the basis of reference quality Helmholtz energy equations of state by Lemmon et al.[20] and Wagner and Pruß[21] that are available for these substances.[22] These fluids were chosen since they envelop the density range of vinyl chloride.

For calibration, the density of propane and water at different state points was fitted as a function of the measured oscillation period, temperature and pressure.[16] A third order Legendre polynomial containing ten coefficients was used for this purpose

$$
\begin{aligned}
\rho \;=\;& a + b_1\underline{T} + c_1\underline{p} + d_1\underline{s} + b_2\frac{\left(3\underline{T}^2 - 1\right)}{2} + d_2\frac{(3\underline{s}^2 - 1)}{2} \\
&+ b_1 d_1\underline{Ts} + b_1 d_2\underline{T}\frac{(3\underline{s}^2 - 1)}{2} + c_1 d_2\frac{(3\underline{s}^2 - 1)}{2} \\
&+ b_1 c_1 d_1\underline{Tps}.
\end{aligned}
\tag{1}
$$

Therein, $\underline{T}$, $\underline{p}$ and $\underline{s}$ are scaled parameters used to enhance the performance of the polynomial, defined by

$$
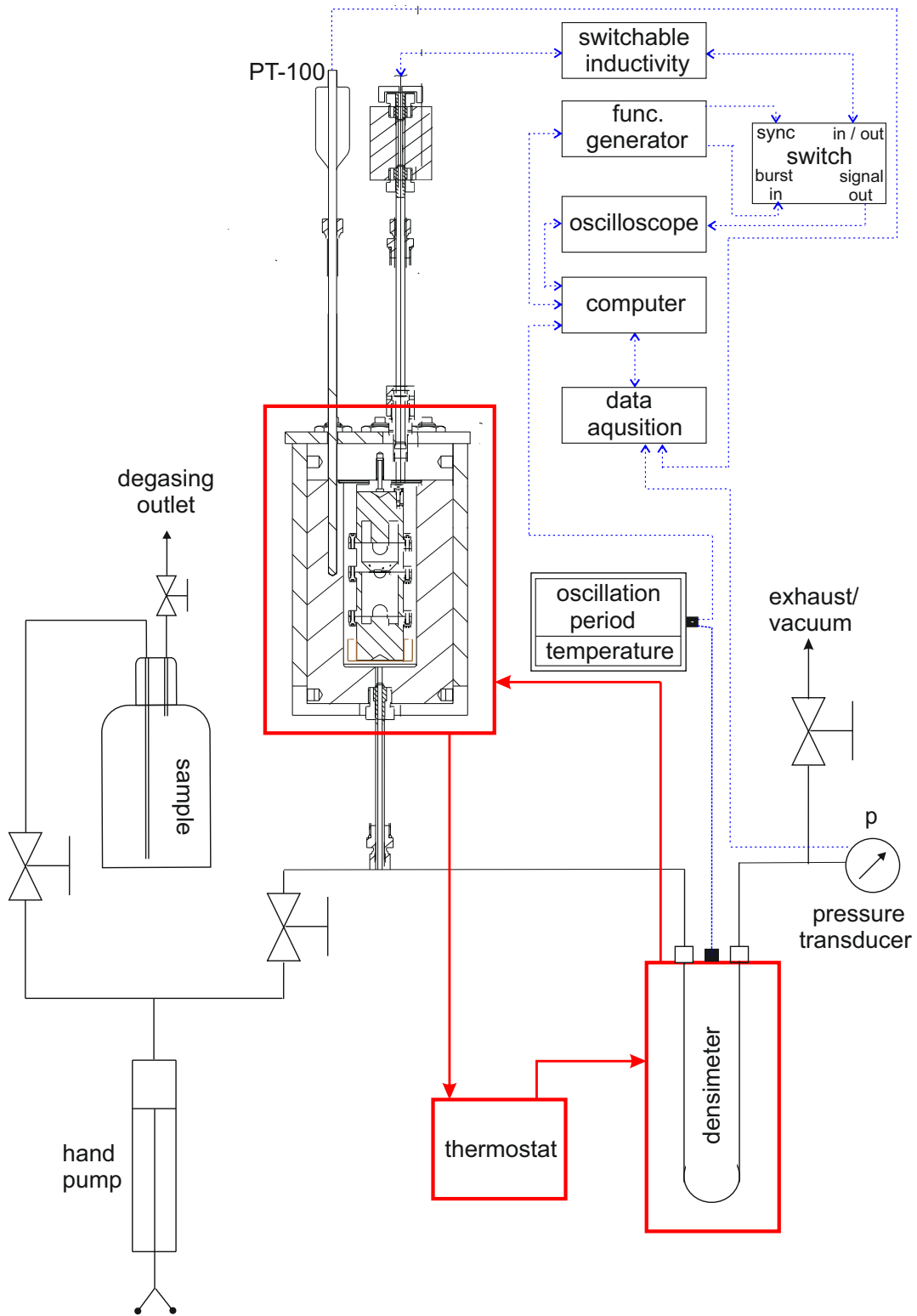\underline{y} = \frac{y - \overline{y}}{\delta y}.
\tag{2}
$$

Figure 2: Schematic of the apparatus for measuring density and speed of sound along with the instruments for control and analysis.

Table 1: Experimental density and the speed of sound data for vinyl chloride, where N is the number of measured data points, $T_{\min} - T_{\max}$ the temperature range and $p_{\max}$ the maximum pressure.

author	year	N	$T_{\min}$- $T_{\max}$/K	$p_{\max}$/MPa	$U_\rho/(\text{kg m}^{-3})$	$U_w/(\text{m s}^{-1})$
density						
Dana et al. [7]	1927	7	260 - 333	vapor pressure	0.7	–
Mizutani and Yamashita[8]	1950	27	222 - 259	vapor pressure	–	–
Dreisbach[9]	1952 - 1955	3	243 - 253	vapor pressure	–	–
Anonymous[10]	1965	1	260	vapor pressure	–	–
Hannaert et al. [11]	1967	2	213 - 233	vapor pressure	8.3	–
Cullick and Ely[12]	1982	68	281 - 337	4.2	0.4	–
de Loos et al. [13]	1983	16	273 - 423	vapor pressure	1.4	–
Zerfa and Brooks[14]	1996	1	328	0.9	–	–
this work	2019	107	283.3 - 362.2	91.07	1.1	–
speed of sound						
this work	2019	109	283.97 - 361.1	91.06	–	1.1

Table 2: Specification of the materials and their suppliers.

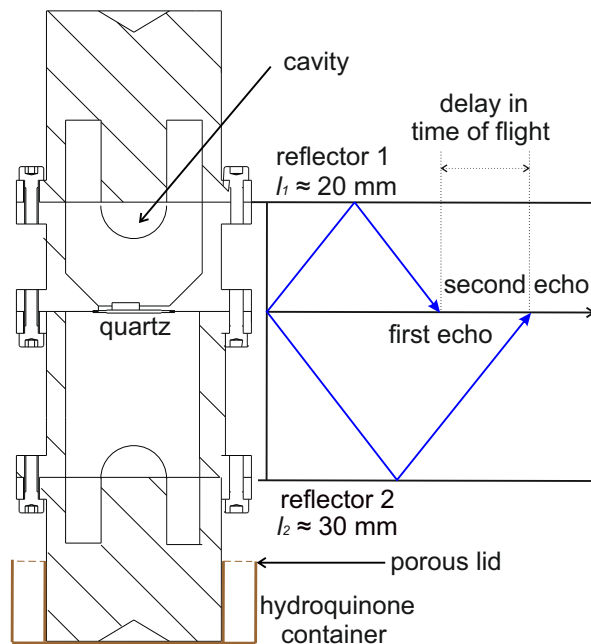| chemical name	CAS number	source	purity/%	purification method
hydroquinone	123-31-9	Sigma-Aldrich	100.00	none
propane	74-98-6	Gerling Holz & Co.	99.50	none
vinyl chloride	75-01-4	Sigma-Aldrich	99.96	none
water	7732-18-5	Merck	99.99	none

Figure 3: Working principle of the speed of sound measurement.

The parameters of the calibration equation (1) are listed in Table 3. A comparison of the calibration measurements with the reference equations of state for propane and water is presented in Figure 4. In the liquid region, these equations of state have very low uncertainties of 0.01% for propane and 0.003% for water. It is convincing that the calibration measurements are in very good agreement with the equations of state, exhibiting a maximum deviation of less than 0.04% for propane and about 0.01% for water. Also at elevated pressures, present measurements are consistent with the reference equations.

Table 3: Parameters of the calibration equation (1) for the density measurement.

parameter	value	unit
a	750.0756	–
b_1	−359.6746	–
c_1	−4.9587	–
d_1	767.7276	–
b_2	−2.7453	–
d_2	1.4900	–
$b_1 d_1$	−14.0967	–
$b_1 d_2$	2.0918	–
$c_1 d_2$	−3.6169	–
$b_1 c_1 d_1$	4.2310	–
$\overline{T}$	57.077	°C
δT	80	°C
$\overline{p}$	46.059	MPa
δp	47.0	MPa
$\overline{s}$	2646.468	μs
δs	60	μs

2.4   Speed of sound measurement

The thermodynamic speed of sound was measured with a double path length pulse-echo technique.[23–26] To bring this method into practice, an 8 MHz gold plated piezoelectric quartz crystal was placed symmetrically between two metallic reflectors of unequal lengths. The quartz was excited electrically with a functional generator (Agilent 33220A). Consequently, two sound waves emerged, traveled in opposite directions, and after reflection, were received back by the quartz at different time instances. These echoes were analyzed with an oscil-
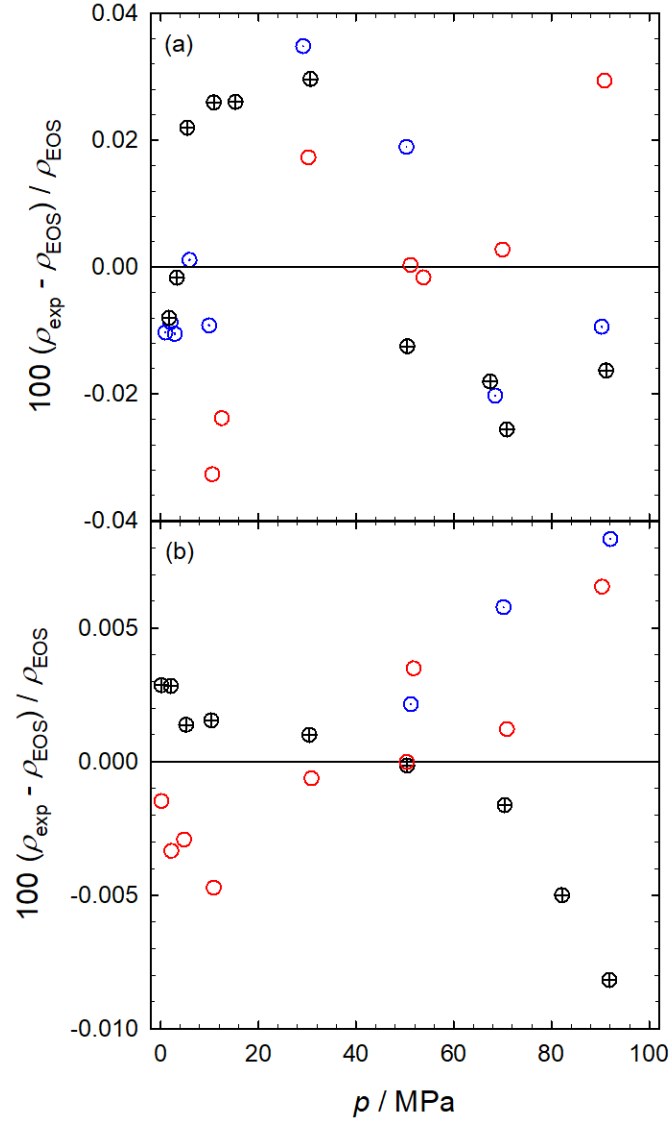
Figure 4: Comparison of the calibration measurements for density as a function of pressure along isotherms: ⊙ 298 K, ⊕ 323 K, ◯ 362 K; (a) propane, where the baseline is the equation of state by Lemmon et al.;[20] (b) water, where the baseline is the equation of state by Wagner and Pruß.[21]

loscope (Agilent DSO1022A) and, neglecting diffraction and dispersion effects, the speed of sound was calculated by

$$w = \frac{2\Delta L}{\Delta t}, \tag{3}$$

where ΔL is the path length difference between the two reflectors and Δt is the delay in time of flight of the two echoes.

The path length difference $\Delta L\,(T_0, p_0) = 9.99$ mm at $T_0 = 300$ K and $p_0 = 1$ MPa was determined from calibration measurements with water. In order to achieve this, the equation of state by Wagner and Pruß [21] was employed, which has an uncertainty of 0.005% for the speed of sound calculation at the selected state point. Thermal expansion and pressure compression of the acoustic cell, fabricated from stainless steel (type 1.4571) were considered by

$$\Delta L(T, p) = \Delta L\,(T_0, p_0) \left[1 + \overline{\alpha} - \frac{1}{E}\,(1 - 2\nu)\,(p - p_0) \right]. \tag{4}$$

Therein, $\nu = 0.3$ is the Poisson number, provided by the steel supplier. The integral thermal expansion coefficient $\overline{\alpha}$ was calculated by

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

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}.[27] The temperature dependent modulus of elasticity E contributed with a first order polynomial

$$E = a + b(T), \tag{6}$$

where $a = 219711.07$ MPa^{-1} and $b = -79.8$ K^{-1} MPa^{-1}.[27]

To measure the delay in time of flight, a peak-to-peak measurement method, which considers the time difference between maximum amplitudes of both echoes, and a correlation approach, were adapted. For the correlation method, a time domain analysis was performed, in which two data cuts were made for both echoes and the delay in time of flight was determined by applying a correlation function. Details were recently described by Javed et al.[28]
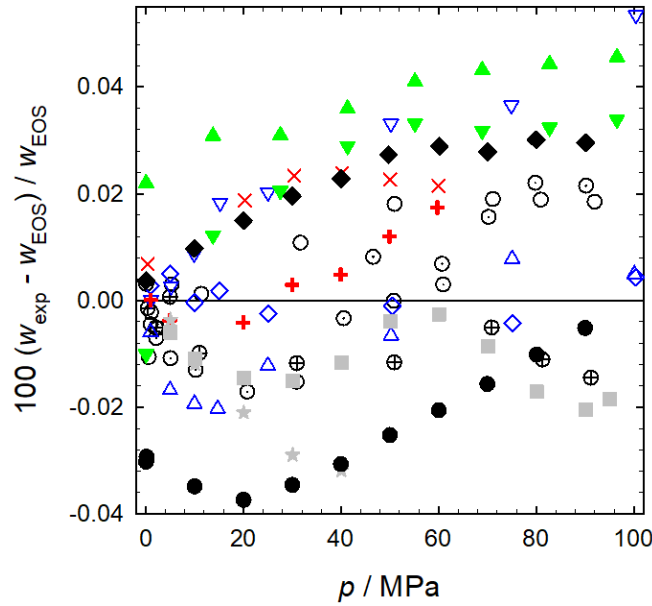

Figure 5: Comparison of the calibration measurements for speed of sound with the equation of state by Wagner and Pruß.[21] Experimental data: this work, ⊙ 298 K, ⊕ 323 K, ◯ 361 K; Lin and Trusler,[29] △ 303 K, ◇ 323 K, ▽ 373 K; Al Ghafri et al.,[30] + 306 K, × 358 K; Wilson,[31] ▲ 303 K, ▼ 364 K; Yebra et al.,[32] ■ 303 K, ★ 323 K; Benedetto et al.,[33] ● 303 K, ◆ 364 K.

A comparison of the calibration measurements with the equation of state by Wagner and Pruß[21] and the experimental literature data is shown in Figure 5. The literature data have a maximum uncertainty of about 0.04%. It should be noted that the calibration measurements of this work are in very good agreement with the equation of state, exhibiting a maximum deviation of 0.02% for the entire measured temperature and pressure range.

3 Results and discussion

Vinyl chloride was delivered in a metal flask as a saturated liquid at ambient temperature and 0.4 MPa pressure. To measure its density and speed of sound, the apparatus was evacuated for about 2 h and the system temperature was reduced to 283 K. Subsequently, vinyl chloride was imbibed into the apparatus and a pressure was specified with the hand pump. Density and speed of sound were measured along nine isotherms between 283 K and 362 K with an increment of 10 K up to a pressure of 91 MPa. The sample fluid was given an equilibration time of about 1.25 h, before measuring the next state point.

3.1 Density

The numerical density data for vinyl chloride together with their uncertainties are listed in Table 4. The overall expanded uncertainty at a confidence level of 95% was calculated by considering the individual uncertainties of temperature u_T, pressure u_p, oscillation period u_s, calibration u_{cal} and impurities u_{imp}

$$U_\rho = k \left[\left(\frac{\partial \rho}{\partial T} \right)_{p,s}^2 u_T^2 + \left(\frac{\partial \rho}{\partial p} \right)_{T,s}^2 u_p^2 + \left(\frac{\partial \rho}{\partial s} \right)_{T,p}^2 u_s^2 + u_{\mathrm{cal}}^2 + u_{\mathrm{imp}}^2 \right]^{1/2}, \qquad (7)$$

with the coverage factor $k = 2$. The partial derivatives of density with respect to temperature and pressure were calculated with the Helmholtz energy equation of state by Thol and Span.[17] The partial derivative with respect to oscillation period was obtained from equation (1). A detailed uncertainty budget for the density measurement is provided in Table 5. It should be noted that the major contribution to the overall uncertainty, i.e. 0.109%, is due to calibration, which also includes reproducibility of the data and aging of the densimeter.

The graphical presentation of experimental uncertainty as a function of pressure along different isotherms is provided in Figure 6. The uncertainty varies between 0.11% to 0.15% for the entire measured temperature and pressure range. The maximum uncertainty is at
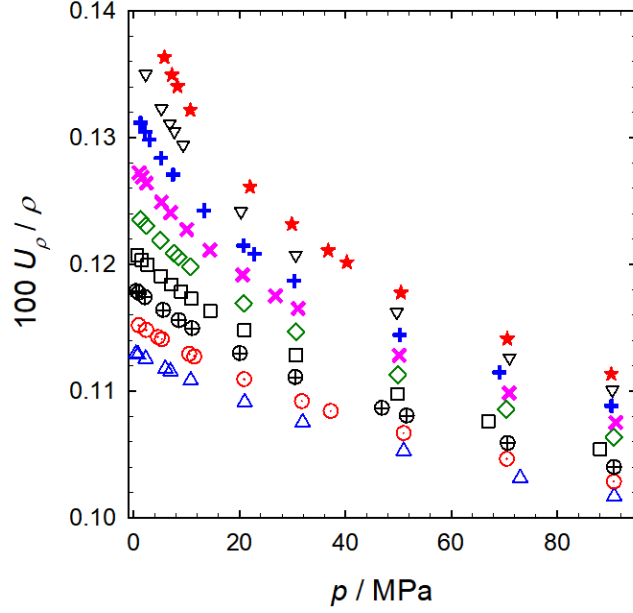
Figure 6: Experimental uncertainty of the density of vinyl chloride as a function of pressure along different isotherms: △ 283 K, ⊙ 293 K, ⊕ 303 K, □ 313 K, ◇ 323 K, × 333 K, + 343 K, ▽ 352 K, ★ 362 K.

262 K and 5.8 MPa.

Table 4: Density of vinyl chloride with its expanded experimental uncertainty for varying temperature T and pressure p[1]

T/K	p/MPa	$\rho/(\mathrm{kg\ m^{-3}})$	$U_\rho/(\mathrm{kg\ m^{-3}})$	T/K	p/MPa	$\rho/(\mathrm{kg\ m^{-3}})$	$U_\rho/(\mathrm{kg\ m^{-3}})$
283.3	0.44	927.8	1.1	322.8	10.69	877.4	1.1
283.3	0.83	928.4	1.1	322.9	20.78	898.4	1.1
283.3	2.27	931.1	1.1	322.9	30.62	915.7	1.1
283.3	5.98	937.6	1.1	322.9	49.89	943.5	1.1
283.3	6.95	939.2	1.1	322.9	70.36	967.7	1.1
283.3	10.76	945.4	1.1	322.9	90.68	988.1	1.1
283.3	20.97	960.4	1.1	332.7	1.03	830.6	1.1
283.3	31.91	974.6	1.1	332.7	1.61	832.6	1.1
283.3	51.01	996.1	1.1	332.8	2.4	835.3	1.1

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Table 4 : (Continued)

T/K	p/MPa	$\rho/(\text{kg m}^{-3})$	$U_\rho/(\text{kg m}^{-3})$	T/K	p/MPa	$\rho/(\text{kg m}^{-3})$	$U_\rho/(\text{kg m}^{-3})$
283.3	73	1017	1.1	332.8	5.24	844.3	1.1
283.3	90.77	1031.9	1.1	332.7	6.95	849.4	1.1
293.2	0.96	910.5	1.1	332.7	10.02	857.8	1.1
293.2	2.4	913.4	1.1	332.7	14.4	868.7	1.1
293.2	4.6	917.8	1.1	332.7	20.56	882.2	1.1
293.2	5.31	919.1	1.1	332.7	26.77	894.3	1.1
293.2	10.5	928.5	1.1	332.7	31.05	902	1.1
293.2	11.45	930.2	1.1	332.7	50.18	931.3	1.1
293.2	20.89	945.2	1.1	332.7	70.92	957	1.1
293.2	31.77	960.3	1.1	332.7	91.07	977.9	1.1
293.2	37.25	967.1	1.1	342.6	1.28	808.6	1.1
293.2	51.02	983.2	1.1	342.6	2.15	812.1	1.1
293.2	70.5	1002.8	1.1	342.6	3	815.5	1.1
293.2	90.71	1020.6	1.1	342.6	5.17	823.5	1.1
303.1	0.52	890.6	1.1	342.6	7.43	831	1.1
303.1	0.98	891.7	1.1	342.5	13.31	848.2	1.1
303.1	2.09	894.2	1.1	342.6	20.72	866.4	1.1
303.2	5.56	901.6	1.1	342.6	22.8	871	1.1
303.1	8.52	907.9	1.1	342.6	30.32	886.1	1.1
303.1	11.08	912.8	1.1	342.6	50.28	918.8	1.1
303.1	20.08	928.5	1.1	342.5	69.08	943.4	1.1
303.1	30.52	944.3	1.1	342.5	90.25	966.7	1.1
303.2	46.93	965.5	1.1	352.4	2.27	788.8	1.1
303.1	51.59	971	1.1	352.4	5.25	802	1.1

Table 4 : (Continued)

T/K	p/MPa	$\rho/(\text{kg m}^{-3})$	$U_\rho/(\text{kg m}^{-3})$	T/K	p/MPa	$\rho/(\text{kg m}^{-3})$	$U_\rho/(\text{kg m}^{-3})$
303.2	70.65	991.1	1.1	352.4	6.81	808.2	1.1
303.2	90.72	1009.5	1.1	352.4	7.68	811.4	1.1
313.0	0.67	871.5	1.1	352.4	9.33	817.3	1.1
313.0	1.54	873.7	1.1	352.4	20.25	849	1.1
313.0	2.58	876.5	1.1	352.4	30.6	872	1.1
313.0	5.13	882.6	1.1	352.4	49.71	905.4	1.1
313.0	7.13	887.2	1.1	352.4	70.97	934.4	1.1
313.0	8.96	891.3	1.1	352.4	90.4	956.4	1.1
313.0	10.88	895.4	1.1	362.3	5.8	781	1.1
313.0	14.47	902.7	1.1	362.3	7.24	787.6	1.1
313.0	20.92	914.5	1.1	362.2	8.28	792.5	1.1
313.0	30.6	930.2	1.1	362.2	10.7	802.1	1.1
313.0	49.8	956.3	1.1	362.2	21.95	836.9	1.1
313.0	66.99	975.9	1.1	362.2	29.87	855.8	1.1
313.0	88.11	996.6	1.1	362.2	36.77	869.9	1.1
322.8	1.26	852.8	1.1	362.3	40.28	876.5	1.1
322.8	2.31	855.9	1.1	362.2	50.5	894.1	1.1
322.8	5.02	863.4	1.1	362.2	70.57	922.8	1.1
322.8	7.6	870.1	1.1	362.2	90.22	946.1	1.1
322.8	8.46	872.1	1.1				

[1] U_ρ is the expanded uncertainty of the density at a confidence level of 95% ($k = 2$), composed of standard uncertainties of temperature $u_T = 0.1$ K, pressure $u_p = 0.002$ MPa, oscillation period $u_s = 0.015$ μs, calibration $u_{\text{cal}} = 0.5$ kg m^{-3} and impurities $u_{\text{imp}} = 0.2$ kg m^{-3}.
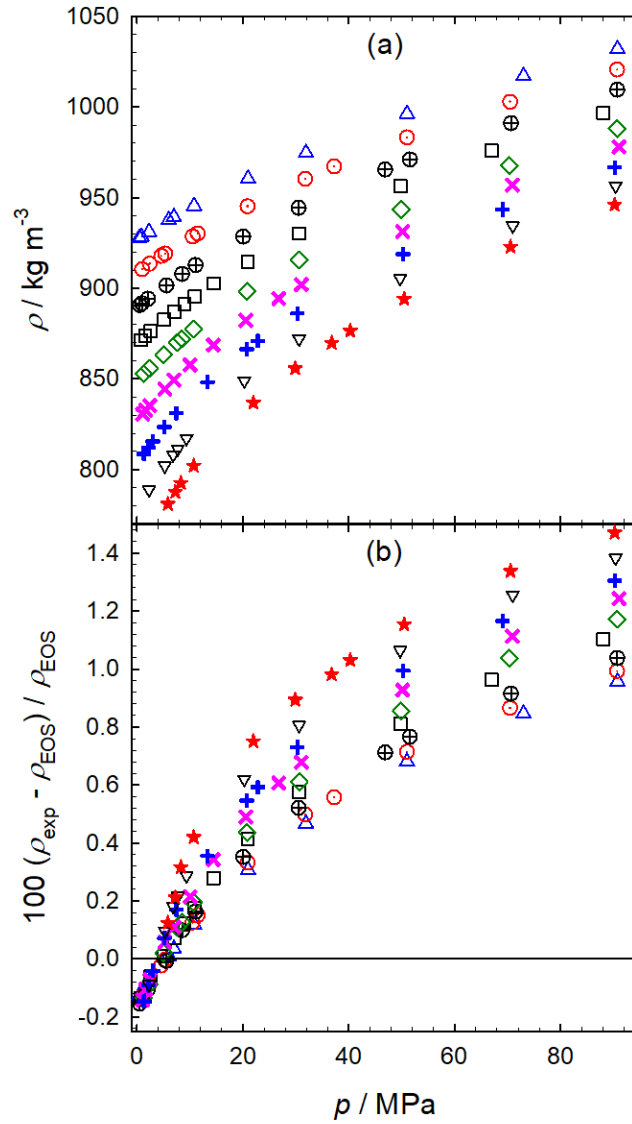
Figure 7: Density of vinyl chloride as a function of pressure (a) and deviation of the density data from the equation of state by Thol and Span[17] (b): △ 283 K, ⊙ 293 K, ⊕ 303 K, □ 313 K, ◇ 323 K, × 333 K, + 343 K, ▽ 352 K, ★ 362 K.

The density of vinyl chloride as a function of pressure along the measured isotherms is depicted in Figure 7(a). The density ranges from 781.0 kg m^{-3} to 1031.9 kg m^{-3} and increases with falling temperature or rising pressure. Deviations of the density data from the Helmholtz energy equation of state by Thol and Span[17] are shown in Figure 7(b). It can be noted that performance of the equation of state is much better at low temperature and low pressure, were the deviations converge to -0.15%. At high pressures, the isotherms systematically diverge from the equation of state. The maximum deviation is 1.5% at the state point 362.2 K and 90.22 MPa. The experimental data at elevated temperatures and pressures indicate that the equation of state should be improved.

A comparison of the present density data with the experimental literature data is provided in Figure 8 and the base line is calculated with the equation of state of Thol and Span.[17] Cullick and Ely[12] as well as Zerfa and Brooks[14] have measured the density of vinyl chloride above its vapor pressure, where the latter authors have measured only a single data point. This point has a deviation of -0.18% from the equation of state. Cullick and Ely[12] have reported the density along six isotherms, covering the temperature range between 281 K and 337 K with a pressure of up to 4.2 MPa. These data are in good agreement with the present work and show a similar trend. Their measurements exhibit a systematic behavior, where all isotherms cross the base line at a pressure between 2 MPa to 4 MPa with a maximum deviation of 0.1%, except for the isotherm 337 K, which has a noticeably different slope with a maximum deviation of about 1.6%.

Table 5: Detailed uncertainty budget for the density measurement of vinyl chloride.

source	type	measuring range	standard uncertainty	density derivative[a]	relative expanded uncertainty[a]
temperature	–	–	0.1 K	1.5 kg m^{-3} K^{-1}	0.016%
pressure	Keller-PAA-33X	<100 MPa	0.02 MPa	0.2 kg m^{-3} MPa^{-1}	0.003%
oscillation period	–	–	0.015 μs	1.3 10^{-7} kg m^{-3} s^{-1}	0.028%
calibration	–	–	0.5 kg m^{-3}	–	0.109%
impurities	–	–	0.2 kg m^{-3}	–	0.044%

[a] Uncertainty value at a typical state point of $T = 322.87$ K and $p = 30.62$ MPa for the present density measurement of vinyl chloride.
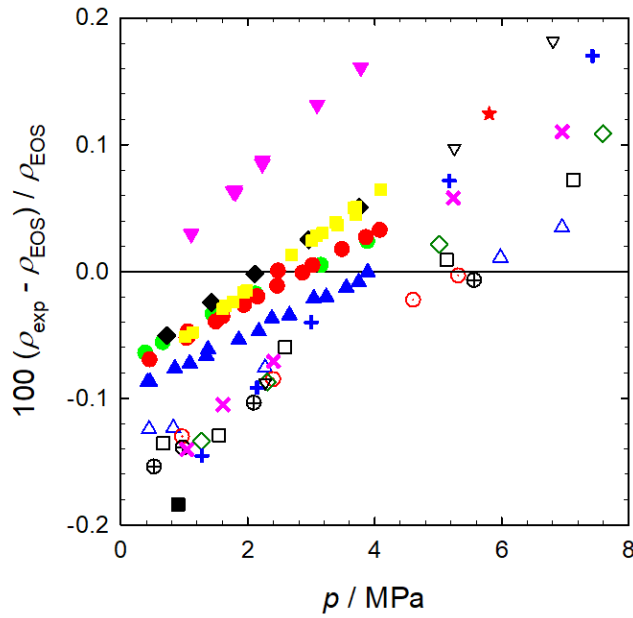
Figure 8: Deviation of the density data from the equation of state by Thol and Span[17] in a region where other experimental data were available: this work; △ 283 K, ⊙ 293 K, ⊕ 303 K, □ 313 K, ◇ 323 K, × 333 K, + 343 K, ▽ 352 K, ★ 362 K: experiment literature data; Cullick and Ely[12] ▲ 281 K, ● 289 K, ● 295 K, ◆ 306 K, ■ 318 K, ▼ 337 K; Zerfa and Brooks[14] ■ 328 K.

3.2 Speed of sound

Speed of sound data for vinyl chloride at different temperatures and pressures with uncertainty values are numerically listed in Table 6. The overall expanded uncertainty of the speed of sound at a confidence level of 95% ($k = 2$) consists of standard uncertainties of temperature u_T, pressure u_p, delay in time of flight $u_{\Delta t}$ and path length difference $u_{\Delta L}$ measurement

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

The partial derivatives of speed of sound with respect to temperature and pressure were calculated with the equation of state for vinyl chloride,[17] while the derivatives with respect to delay in time of flight and path length difference were calculated from equation (3). A detailed uncertainty budget for the speed of sound measurement at a typical state point is provided in Table 7. The expanded uncertainties of temperature, pressure and timing are below 0.02%. The largest contribution to the overall uncertainty is due to path length calibration, i.e. 0.08%, which includes a margin for reproducability of the calibration data at elevated temperatures and pressures. A graphical representation of the uncertainties shows that the overall expanded uncertainties are below 0.16% for the entire measured data set, cf. Figure 9. At pressures above 20 MPa, the uncertainties are below 0.1% throughout. As with the density data, uncertainties are large at high temperatures and low pressures because the speed of sound changes significantly in this region, cf. Figure 10(a).

The speed of sound of vinyl chloride as a function of pressure along nine isotherms is shown in Figure 10(a). It was measured over a wide span from 550.9 m s^{-1} to 1336.2 m s^{-1}. A comparison of the present experimental data with the preliminary equation of state by Thol and Span[17] is shown in Figure 10(b). It should be noted that no experimental caloric data, e.g., speed of sound or heat capacity, were available in the literature when the equation
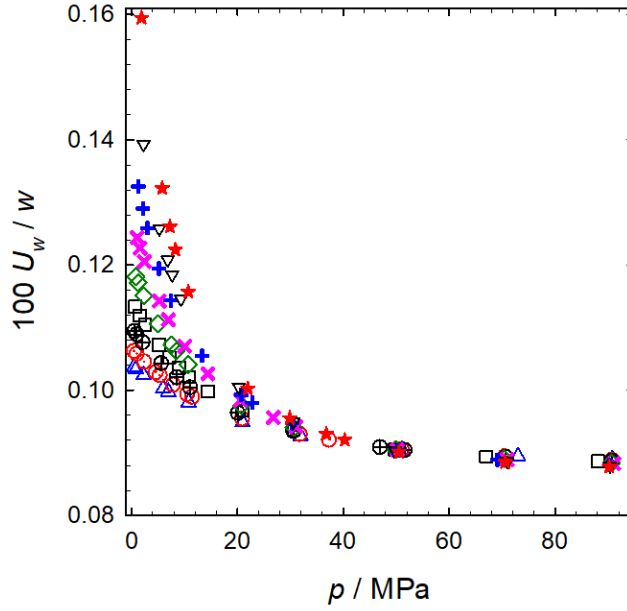
Figure 9: Experimental uncertainty of the speed of sound of vinyl chloride as a function of pressure along isotherms: △ 284 K, ⊙ 294 K, ⊕ 303 K, □ 313 K, ◇ 323 K, × 333 K, + 342 K, ▽ 351 K, ★ 361 K.

of state of Thol and Span[17] was developed. As a consequence, the equation of state deviates by up to -12.4% from the present experimental data. The divergence is high at low pressures for all isotherms. However, at high pressures, all isotherms are systematically approaching the equation of state with a minimum deviation of -7.5%.

Table 6: Speed of sound of vinyl chloride with its expanded experimental uncertainty for varying temperature T and pressure p.[1]

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})
283.96	0.45	935.3	1.0	322.48	8.46	817.3	0.9
283.82	0.83	938.4	1.0	322.49	10.69	835.6	0.9
283.97	2.27	948.1	1.0	322.61	20.78	907.9	0.9
283.85	5.98	973.3	1.0	322.62	30.62	968.1	0.9
283.92	6.96	979.5	1.0	322.64	49.89	1066.7	1.0
283.86	10.77	1003.2	1.0	322.64	70.35	1153.5	1.0

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})
283.87	20.97	1060.5	1.0	322.64	90.67	1228.0	1.1
283.86	31.90	1114.8	1.0	332.33	1.03	697.8	0.9
283.87	51.01	1197.1	1.1	332.33	1.61	704.5	0.9
283.95	73.00	1278.1	1.1	332.35	2.40	713.4	0.9
283.95	90.77	1336.2	1.2	332.33	5.24	743.4	0.8
293.75	0.49	888.2	0.9	332.12	6.95	760.5	0.8
293.53	0.97	891.4	0.9	332.12	10.02	788.6	0.8
293.52	2.40	903.0	0.9	332.13	14.40	824.9	0.8
293.50	4.61	919.3	0.9	332.13	20.56	870.5	0.9
293.52	5.31	924.3	0.9	332.20	26.77	911.4	0.9
293.76	7.84	940.1	0.9	332.18	31.05	937.6	0.9
293.51	10.50	959.4	1.0	332.20	50.18	1038.8	0.9
293.52	11.45	965.5	1.0	332.21	70.92	1129.2	1.0
293.53	20.89	1021.6	1.0	332.22	91.06	1204.5	1.1
293.53	31.77	1078.3	1.0	341.91	1.28	649.9	0.9
293.63	37.25	1104.4	1.0	341.93	2.15	661.1	0.9
293.54	51.02	1164.7	1.1	341.92	2.99	671.9	0.8
293.63	70.49	1239.5	1.1	341.94	5.17	697.2	0.8
293.65	90.70	1307.8	1.2	341.93	7.43	721.5	0.8
303.22	0.52	840.6	0.9	341.82	13.32	776.7	0.8
303.28	0.98	844.2	0.9	341.84	20.72	835.7	0.8
303.30	2.08	853.5	0.9	341.84	22.80	850.9	0.8
303.36	5.59	881.1	0.9	341.85	30.31	900.7	0.9
303.22	8.52	903.1	0.9	341.86	50.27	1010.8	0.9

Table 6 : (Continued)

T/K	p/MPa	$w/(\mathrm{m\ s}^{-1})$	$U_w/(\mathrm{m\ s}^{-1})$	T/K	p/MPa	$w/(\mathrm{m\ s}^{-1})$	$U_w/(\mathrm{m\ s}^{-1})$
303.23	11.08	921.1	0.9	341.87	69.07	1095.7	1.0
303.23	20.07	978.5	0.9	341.88	90.24	1177.5	1.0
303.24	30.52	1036.5	1.0	351.50	2.27	612.1	0.9
303.34	46.93	1115.0	1.0	351.51	5.25	652.1	0.8
303.26	51.59	1135.3	1.0	351.49	6.81	670.9	0.8
303.35	70.65	1210.7	1.1	351.51	7.68	680.8	0.8
303.36	90.72	1280.4	1.1	351.49	9.34	698.9	0.8
313.08	0.67	792.9	0.9	351.52	20.26	797.5	0.8
312.84	1.54	801.7	0.9	351.46	30.59	871.0	0.8
313.08	2.57	810.4	0.9	351.48	49.70	980.3	0.9
312.86	5.13	833.2	0.9	351.50	70.98	1078.5	1.0
312.86	7.13	849.6	0.9	351.53	90.39	1154.6	1.0
312.85	8.96	863.9	0.9	361.21	1.89	550.9	0.9
312.86	10.88	878.4	0.9	361.17	5.80	611.6	0.8
312.89	14.47	903.8	0.9	361.10	7.24	631.0	0.8
312.91	20.92	945.9	0.9	361.04	8.27	644.0	0.8
312.91	30.59	1002.2	0.9	361.05	10.71	672.1	0.8
312.92	49.80	1096.6	1.0	361.07	21.95	776.4	0.8
312.92	66.99	1168.2	1.0	361.08	29.86	835.3	0.8
312.91	88.10	1245.1	1.1	361.05	36.77	880.1	0.8
322.73	0.82	745.5	0.9	361.11	40.28	901.4	0.8
322.48	1.27	750.4	0.9	361.08	50.50	957.7	0.9
322.49	2.31	761.0	0.9	361.10	70.56	1052.6	0.9
322.50	5.02	787.0	0.9	361.13	90.22	1131.4	1.0

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})
322.49	7.59	810.0	0.9				

[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 $u_T = 0.05$ 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.

Table 7: Detailed uncertainty budget for the speed of sound measurement of vinyl chloride.

source	type	measuring range	standard uncertainty	speed of sound derivative[a]	relative expanded uncertainty[a]
temperature	PT-100	84 - 693 K	0.05 K	4.2 m s^{-1} K^{-1}	0.017%
pressure	Keller-PAA-33X	<100 MPa	0.02 MPa	0.6 m s^{-1} MPa^{-1}	0.012%
time	oscilloscope Agilent DSO1022A	–	0.002 μs	$4.7 \cdot 10^7$ m s^{-2}	0.019%
path length	–	–	7 μm	$4.8 \cdot 10^4$ s^{-1}	0.080%

[a] Uncertainty value at a typical state point of $T = 322.62$ K and $p = 30.6$ MPa for the present speed of sound measurement of vinyl chloride.

4   Conclusions

An apparatus was built to simultaneously measure the density and speed of sound of vinyl chloride. An Anton Paar densimeter was employed for the density measurement and was calibrated with propane and water. The maximum deviation of the density calibration measurements was 0.04% from the reference quality equation of state for propane by Lemmon et al.[20] and 0.01% from the reference quality equation of state for water by Wagner and Pruß.[21] For the speed of sound measurements, a double path length pulse-echo technique was implemented and the acoustic cell was calibrated with water. The calibration measurements have a maximum deviation of 0.02% from the equation of state by Wagner and Pruß.[21]

Density and speed of sound of vinyl chloride were investigated over a wide temperature range from 283 K to 362 K up to a pressure of 91 MPa. A detailed experimental uncertainty analysis was carried out. The maximum expanded uncertainty, at a confidence level of 95%
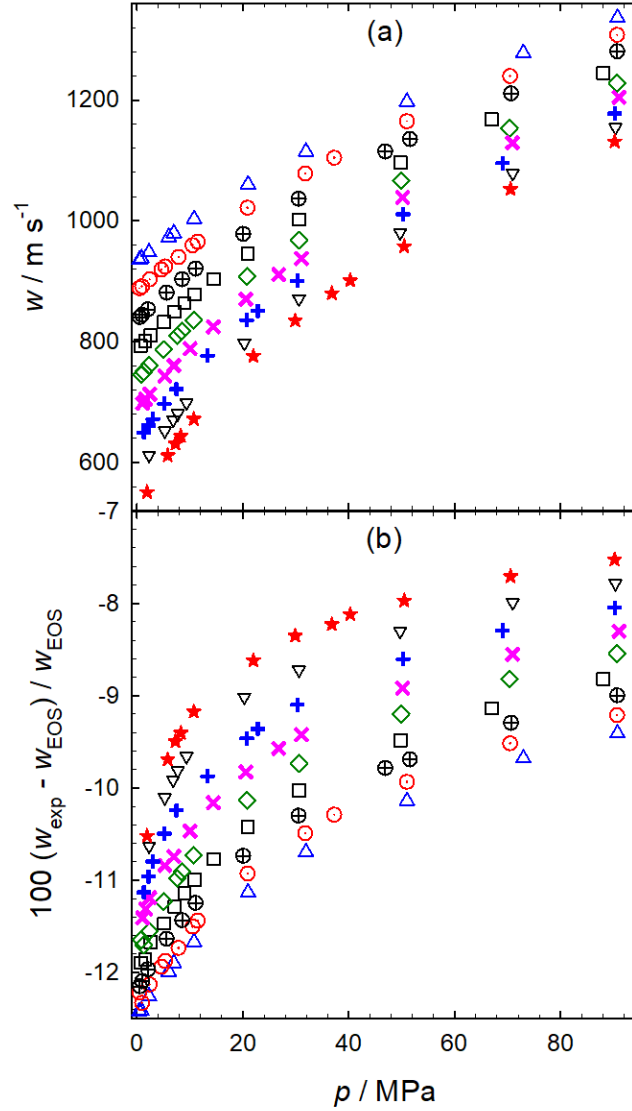
Figure 10: Speed of sound of vinyl chloride (a) and deviation of the present data from the equation of state by Thol and Span[17] (b): △ 284 K, ⊙ 294 K, ⊕ 303 K, □ 313 K, ◇ 323 K, × 333 K, + 342 K, ▽ 351 K, ★ 361 K.

$(k = 2)$, is 1.1 kg m^{-3} for the density and 1.2 m s^{-1} for the speed of sound measurements. Present results for the density of vinyl chloride were compared with the available literature data and the preliminary equation of state by Thol and Span.[17] Only two authors have reported the density above the vapor pressure, i.e. Cullick and Ely[12] as well as Zerfa and Brooks.[14] Present data are in a good agreement with these literature data and have a maximum deviation of 1.5% from the equation of state. However, for the speed of sound of vinyl chloride, no literature data were found and the preliminary equation of state of Thol and Span[17] diverges up to -12.4% from the present data. Therefore, the preliminary equation of state for vinyl chloride should be refined on the basis of the present data.
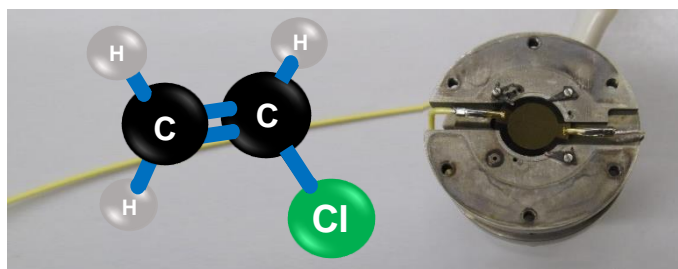
5   Acknowledgement

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