Ultrasonic Parameters as a Function of Absolute Hydrostatic Pressure. II. Mathematical Models of the Speed of Sound in Organic Liquids

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Polynomial expressions for the speed of sound as a function of pressure for 68 different organic liquids are presented in tabular form. (The liquids form a subset of those discussed in the companion paper: Ultrasonic parameters as a function of absolute hydrostatic pressure. I. A review of the data for organic liquids.) The polynomial expressions are based upon the experimental results reported by many different researchers. For some common liquids, such as benzene, hexane, ethanol, and carbon tetrachloride, the results of as many as five different researchers are reported. These results sometimes vary widely—far more than would be expected from calculated experimental uncertainties. An analysis is presented of how well pressure-dependent polynomials fit the experimental data when the number of coefficients is increased. The error in the polynomial fit is also explored when both pressure and temperature dependencies are present. Finally, differences between ultrasonic and Brillouin scattering experimental results are discussed. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1555589]

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1. Introduction

Over the past century, hundreds of researchers have expended great effort to precisely determine the effect of fluid pressure on the speed of sound in organic liquids. As a consequence, a great deal of fragmented information exists in the literature about the topic. However, there seems to be a lack of a unified theory, and no comprehensive review exists that broadly categorizes the experimental results and allows for the comparison of these results and their use in related or similar settings. This paper attempts to fill this gap, and is intended to serve as a springboard for future comparative studies of the dependence of the speed of sound on the pressure between chemical groups, and other more interdisciplinary research efforts. The article is the second of two covering ultrasonic properties as a function of pressure in organic liquids. Where this second article focuses on mathematical models of the speed of sound as a function of pressure, the first provided a broad overview of the past century's research involving a variety of ultrasonic properties as a function of pressure in organic liquids, including both speed of sound and absorption. (Oakley *et al.*, 2003).

The common approach in the literature of research in this area is to assume that the speed of sound, *c*, depends on the

pressure, p, as a polynomial, i.e., in the form $c(p) = \sum_{i=0}^{n} a_i p^i$, where the a_i are experimentally determined coefficients (here c is the speed of sound in m/s, and p is the pressure in MPa). The heart of this paper consists of a table of these coefficients a_i that can be used to model $c(p)$ at a temperature near 25 °C for various organic liquids. The coefficients were obtained from the work of many researchers; in many cases, the coefficients were calculated for this paper directly from the voluminous experimental data available in the literature. Model inaccuracies are also discussed, along with variations found among experimental results obtained through different techniques for measuring the speed of sound in a given liquid.

2. Background Experimentation and Theory

Speed of sound in liquids is generally measured by two fundamentally different techniques: ultrasonic pulse and Brillouin scattering. The ultrasonic pulse method consists of measuring the time it takes for a short ultrasonic pulse, generally in the range of 1–5 MHz, to pass along a fixed path in a pressurizable container. Sometimes two transducers are used, one as sender and one at the far end as receiver, as in much of the earlier research. In recent decades, the pulse is more commonly reflected and its echo detected by a gated amplifier back at the transducer, which Takagi and Teranishi (1987) dubbed the "sing-around" method. Brillouin scattering, on the other hand, makes use of the Brillouin frequency shift (Λ_s), which is related to the adiabatic acoustic velocity c by the expression

$$c = \frac{\lambda_0 \Delta \nu_s}{\sqrt{2}}, \tag{1}$$

where c is the speed of sound and λ_0 is the wavelength of the laser light. Experimentation is most commonly done in pressure ranges between roughly 0.10 and 200 MPa and temperatures in the range of 20–30 °C. However, some experimental results, especially from the former Soviet block of the 1970s and 1980s, as well as more recent work, approach 10 GPa with a broad range of temperatures.

Most models for the speed of sound are derived from thermodynamic relationships that were originally developed for longitudinal acoustical waves in an idealized fluid [Morse and Ingard (1968)]. This fluid is assumed to be uniform and homogenous in its properties, and to be in thermodynamic equilibrium except for the presumed linear effects of the sound itself. The fluid is characterized by its density Δ, pressure, p, and temperature, T; these three quantities are connected through an equation of state. The equation can either be explicit, as in $pV = nRT$, or in terms of partial derivatives, as in the expression $(\partial \beta / \partial P)_T = -(\partial \kappa_T / \partial T)_P$, where β is the coefficient of thermal expansion and κ_T is the isothermal compressibility. Two partial derivatives frequently used in calculating thermodynamic parameters are those for the isothermal compressibility of fluids:

$$\kappa_T = -\frac{1}{\nu}\left(\frac{\partial \nu}{\partial P}\right)_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right)_T,$$

and the coefficient of thermal expansion

$$\beta = \frac{1}{\nu}\left(\frac{\partial \nu}{\partial T}\right)_P = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P.$$

Both κ_T and β are weakly dependent on p and T. Using κ_T and β, we can compute the other partial derivatives of ρ, p, and T. For example, if p, β, and κ_T are given as functions of ρ and T, then the rate of increase of pressure with temperature at constant volume, α, can be written as $\alpha = (\partial P / \partial T)_\rho = \beta / \kappa_T$. Two final relationships link C_V to C_P: $C_V \kappa_T = C_P \kappa_S$, (also written as $\kappa_T = \gamma \kappa_S$), and $\gamma - 1 = T \beta^2 / \kappa_s C_P \rho$.

The seven thermodynamic variables: pressure, volume, temperature, entropy s, and the three components of the vector fluid velocity **u**, can be related to one another through the equation of state, the equation of energy conservation, and also through the equations of continuity for mass and momentum, and the second law of thermodynamics. Combining these various equations leads to the following commonly used quantities and relationships

$$\kappa_s = \frac{1}{\gamma \rho}\left(\frac{\partial \rho}{\partial p}\right)_T = \frac{1}{\rho c^2}, \tag{2}$$

$$\frac{\beta V T}{C_P} = (\gamma - 1)\frac{\kappa_S}{\beta} = (\gamma - 1)\frac{1}{\rho \beta c^2}. \tag{3}$$

These equations form a summary of many, if not most, of the important relationships used in the field. From Eqs. (2) and (3) in particular, we can clearly see that the speed of sound as a function of pressure is a parameter that can be used to calculate key thermodynamic properties—including adiabatic compressibility, density, and specific heat ratios. These calculations can be more accurate than those obtained from many other methods, as for example, calculating κ_S through knowledge of the partial derivative of density with respect to pressure Eq. (2), or through knowledge of β, V, T, c_P, and γ, as with Eq. (3).

3. Mathematical Models for the Speed of Sound as a Function of Pressure

Obtaining relatively straightforward mathematical models for speed of sound as a function of pressure can clearly simplify the calculation of thermodynamic properties. Somewhat surprisingly, however, empirical mathematical models for the speed of sound of organic liquids vary widely in structure. Linear, cubic root, and series expansions, for example, have been used to model the speed of sound in benzene. Sometimes no analytical model for the speed of sound is presented in the literature; instead, the desired quantity, such as adiabatic compressibility or specific heat ratio, is simply calculated point by point from the measured speed of sound at the indicated pressure.

Some empirical formulas for sound speed as a function of pressure are so complex that their results are difficult to generalize, some models are so simple as to be virtually useless. An example of a complex formula is that of Lainez, Zollweg and Streett (1990), who proposed an equation in which their experimental results for the speed of sound c in *n*-pentane and 2,2-dimethylpropane were fitted as a function of pressure and temperature to a ratio of two polynomials:

$$c^2 = \frac{\Sigma_{i=0}^{m_1} \Sigma_{j=0}^{m_2} a_{i,j}(p-p_0)^i(T-T_0)^j}{\Sigma_{k=0}^{n_1} \Sigma_{l=0}^{n_2} b_{k,l}(p-p_0)^k(T-T_0)^l}. \tag{4}$$

Here p_0 and T_0 are arbitrarily chosen constants within the range of pressure and temperature for which the data was available—they were introduced primarily to reduce the magnitude of the coefficients. The ratio was normalized to make the leading term in the denominator $b_{0,0}=1$. The values of $a_{i,j}$ and $a_{k,l}$ were computed from a least-squares analysis of the experimental data. All measurements were weighted according to an uncertainty determined by assuming that experimental error was derived primarily from two sources: the uncertainty in the pressure measurement whose effect on speed of sound was determined by a preliminary fit of the results along isotherms, and an assumed uncertainty of 0.1 of a cycle in the echo-overlap determination. Upper values $m_1=m_2=n_1=n_2=2$ were selected for both substances to optimize the chi-square of the fitting of the seventeen parameters. Calculations for speed of sound from the above equation reproduced experimental results with a root-mean-square fractional error of 0.036% and 0.046% for *n*-pentane and 2,2-dimethylpropane, respectively, within the estimated accuracy of the speed-of-sound measurements. Measurements were made at pressures up to 210 MPa for pentane and 54 MPa for 2,2-dimethylpropane, and temperatures ranging between 263 and 433 K.

On the other end of the spectrum is an extremely simple equation used to describe speed of sound as a function of pressure by researchers from Eastern Europe:

$$c = \sqrt[3]{c_0^3 + K(p-p_0)}. \tag{5}$$

The cubic root could lead a researcher to suspect a relationship to a cubic form, such as Eyring's liquid free volume theory [Eyring (1936)]. Unfortunately, [Melikhov (1982)] one finds that K is defined as $\partial c^3/\partial P$, which renders Eq. (5) rather useless.

The most commonly used empirical model developed for speed of sound as a function of pressure uses experimental results for the speed of sound to determine the coefficients in a polynomial expression by means of least squares

$$c(p) = \sum_{i=0}^{n} a_i p^i. \tag{6}$$

Here the a_is are the coefficients of the polynomial expression determined for each liquid at a given temperature. Because this is the most straightforward of the various empirical formulas used to model $c(p)$, Eq. (6) was chosen as the "master form" used to fit results from a broad range of organic liquids. Table 1 provides a comparative listing of the a_is for the organic liquids shown, organized in an alphabetical listing by chemical name. As the table reveals, a second order polynomial is generally sufficient to approximate sound speed curves for most experimental data. A more complicated, temperature dependent version of the $c(p)$ relation Eq. (6) is

$$c = \sum_{i=0}^{2} \sum_{j=0}^{4} a_{ij} T^i p^j,$$

with 15 parameters a_{ij} whose values are calculated by least-squares analysis of the experimental data [as, for example, Takagi (1991), Trichlorofluoromethane].

The experimental results used in the table were chosen from among the most accurate published results available for the given liquid. Some results were used because they provided for a comparison between optical and acoustical methods of obtaining speed of sound data. Still other results were chosen because of their known reliability within a given range, or contrarily, because they were the only available results for that particular chemical. In every case, experimental error is provided as calculated by the original authors. Pressure coefficients were generally calculated for temperatures at or about room temperature (25 °C), with exceptions as noted.

4. Discussion

Table 1 is presented in such a fashion that researchers can glean what they may from the data. As Table 2 shows, however, increasing the order of the polynomial from a three coefficient version (a_0,a_1,a_2) to a four coefficient version (a_0,a_1,a_2,a_3) changes the values of the coefficients slightly, so comparison of coefficients between polynomials of different order must be done carefully. (Because of the improvement in the increased fit from three to four coefficients, four coefficients were used wherever practicable.)

Several comments of general interest about Table 1 are called for. The first is the surprising variability in results for the same substance among various researchers. These results are often far outside of the indicated inaccuracies, even given the changes of speed of sound temperature. For example, the a_0 coefficients for benzene range from 1274.1 m/s at 30 °C [Takagi and Teranishi (1982a)] to 1500.0 m/s at 20 °C [Bohidar (1989b)], with uncertainties of 0.3% and 0.5%, respectively. (The derivative of the speed of sound with respect to temperature for benzene is 4.65 m/s per °C [Lide (1993)].) The a_1 coefficients—the most important coefficients in light of the pressure dependency, had even greater ranges. Brown *et al.* (1988), for example, had an a_1 of 2.0 for ethanol, while Bohidar (1989a) had 3.3, and Hawley *et al.* (1970) had 5.1. *n*-hexane had a_1 coefficients of 2.3; 3.3; 6.8; and 8.3 as calculated using data provided by Bohidar (1988), Allegra *et al.* (1970), Hawley *et al.* (1970), and Daridon *et al.* (1998), respectively. These are enormous differences which call to question the accuracy of the experimental apparatus

TABLE 1. Coefficients of polynomial equations of form $c(p) = \sum_{i=0}^{4} a_i p^i$ for the organic liquids. Uncertainties are those noted by the original investigators for their experimental data. Under the 'Technique,' column, if no symbol is given, the original investigators (noted under 'Investigator(s)') calculated and published the a_i's in their own work, and the a_i's are simply presented here as originally calculated

Liquid	Investigator(s)	Pressure (MPa)	Temp. range of original data (°C)	Experimental technique	Modeling technique	Coefficient a_0	a_1	a_2	a_3 (when available)	Uncertainty $< \pm x$	Temp. of data set (°C)
Acetic acid (CH$_3$CO$_2$H)	Bohidar (1989b)	0.1–82.5	20	Brillouin scattering		1140	3	2×10^{-3}		1%	20
Acetone (CH$_3$COCH$_3$)	Bohidar (1989b)	0.1–82.5	20	Brillouin scattering		1180	5	2×10^{-3}		1%	20
Amyl propionate (C$_2$H$_5$CO$_2$C$_5$H$_{11}$)	Guseinov and Klimova (1983)	0.1–50.0	−63–97	pulse echo	a	1233.2	5.4	0		no inaccuracy given	27
Aniline (C$_6$H$_5$NH$_2$)	Takagi (1976)	0.1–210	10–60	ultrasonic pulse (1 MHz)		1623	0.29867	-3.595×10^{-4}		0.2%	30
Aniline (C$_6$H$_5$NH$_2$)	Takagi (1980)	0.1–207	25	pulse echo (1 MHz)		1623	0.29867	-3.595×10^{-5}		0.3%	30
Aniline (C$_6$H$_5$NH$_2$)	Takagi and Teranishi (1985)	0.1–180	30	ultrasonic pulse (1 MHz)		1624.1	3.0	0		0.3%	30
Benzene (C$_6$H$_6$)	Takagi and Teranishi (1987)	0.1–200	10–50	pulse echo (2 MHz)		1298.9	5.0	0		1.8 m/s	25
Benzene	Bohidar (1989b)	0.1–82.5	20	Brillouin scattering		1500	3.6	1×10^{-3}		1%	20
Benzene (C$_6$H$_6$)	Takagi and Teranishi (1982a)	0.1–200	30	ultrasonic pulse (1 MHz)	a	1274.1	4.9	0		0.3%	30
Benzene (C$_6$H$_6$)	Takagi and Teranishi (1982b)	0.1–200 30	30 20–40	pulse echo (1 MHz)	a	1320.7	5.6	−0.1		0.3%	20
Benzonitrile (C$_7$H$_5$N)	Takagi and Teranishi (1988)	0.1–100	25, 30	pulse echo (2 MHz)	a	1416.3	3.7	0		1.8 m/s	25
Bromobenzene (C$_6$H$_5$Br)	Takagi and Teranishi (1982a)	0.1–200	30	ultrasonic pulse (1 MHz)	a	1141.3	3.2	0		0.3%	30
n-Butane (C$_4$H$_{10}$)	Niepmann (1984)	coexistence line-60	−73–102	pulse echo (2 MHz)	a	897.6166	11.1520	−0.0978	0.0006	0.2%	25
n-Butanol (CH$_3$(CH$_2$)$_2$CH$_2$OH)	Carnevale and Litovitz (1955)	0.1–196	0–45	pulse echo (25 MHz)	c	1219.6	5.6	0		0.2	30
n-Butanol (CH$_3$(CH$_2$)$_2$CH$_2$OH)	Hawley et al. (1970)	0.1–489	30	pulse echo (22 MHz region)	a	1254.2	4.7	0		0.3%	30
n-Butanol (CH$_3$(CH$_2$)$_2$CH$_2$OH)	Sysoev and Otpuschennikov (1977)	0.1–860	30	pulse echo (4 MHz)	a	1287.9	4.2	0		0.3%	30
Butylbenzene (CH$_3$(CH$_2$)$_3$C$_6$H$_5$)	Makhno et al. (1985)	0.1–245	40–180	pulse echo (2 MHz)	a	1275.1	4.8	0		0.2%	45
Carbon tetrachloride (CCl$_4$)	Hawley et al. (1970)	0.1–288	30, 75	pulse echo (13.4 MHz region)	a	907.7303	3.9577	−0.0098		0.3%	30
Carbon tetrachloride (CCl$_4$)	Sysoev and Otpuschennikov (1979)	0.1–506	20–180	ultrasonic pulse (5 MHz)	a	938.7612	3.8919	−0.0145		0.3%	20
Carbon tetrachloride (CCl$_4$)	Lainez et al. (1987)	0.1–55	56–136	pulse echo (3 MHz)	a	848.6372	12.2643	−0.0258	−0.0005	0.05%	25
Carbon tetrachloride (CCl$_4$)	Bobik et al. (1979)	coexistence region-62	−8–162	pulse echo (2 MHz)	b	923.9966	4.0175	−0.0164	0.0001	0.5 m/s	25
Carbon tetrachloride (CCl$_4$)	Bohidar (1989a)	0.1–80	20	Brillouin scattering		1020	3.3	1×10^{-3}		1%	20
Chlorobenzene (C$_6$H$_5$Cl)	Takagi and Teranishi (1982a)	0.1–200	30	ultrasonic pulse (1 MHz)	a	1253.4	3.7	0		0.3%	30
Chlorodifluoromethane (CHClF$_2$)	Niepmann et al. (1987)	coexistence line-60	−73–147	pulse echo (2 MHz)	b	532.7416	9.7034	−0.1013	0.0006	0.2%	25
Cyclohexane (C$_6$H$_{12}$)	Takagi (1976)	0.1–210	10–60	ultrasonic pulse (1 MHz)		1230.93	0.62613	-2.326×10^{-4}		0.2%	30

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Liquid	Investigator(s)	Pressure (MPa)	Temp. range of original data (°C)	Experimental technique	Modeling technique	a_0	a_1	a_2	a_3 (when available)	Uncertainty $< \pm x$	Temp. of data set (°C)
1-Decanol ($C_{10}H_{22}O$)	Sysoev (1977)	0.1–101	20–200	pulse echo (5 MHz)	a	1364.2	4.7	0		0.3%	30
Diallyl ether ($C_6H_{10}O$)	Pevnyi (1983)	0.1–800	50–170	ultrasonic pulse (2 MHz)	a	1096.2	4.4	0		0.2%	50
Dibutyl ether ($C_8H_{18}O$)	Pevnyi and Otpuschenikov (1980)	0.1–811	20–170	pulse echo (2 MHz)	a	1219.3	4.2	0		0.2%	20
Dichloromethane (CH_2Cl_2)	Niepmann *et al.* (1987)	coexistence line-60	−73–147	pulse echo (2 MHz)	b	1071.8	3.9	0		0.2%	25
Dichloromethane (CH_2Cl_2)	Takagi (1994)	0.1–50	25–80	pulse echo (2 MHz)	a	1071.1	3.7	0		0.2%	25
1,2-Dichloro-1,2,2-trifluoroethane	Takagi *et al.* (1992)	0.1–75	10–100	pulse echo (2 MHz)	b	704.5549	5.9246	−0.3663	0.0002	0.3%	25
Dichlorotetrafluoroethane (R114) ($CClF_2$–$CClF_2$)	Takagi and Teranishi (1986)	saturated vapor pressure −50	10–50	pulse echo (2 MHz)		549.91	8.0160	−.078957	0.00051965	1.8 m/s	25
Diethyl ether ($C_4H_{10}O$)	Sysoev and Otpuschennikov (1979)	0.1–506	17.5–250	ultrasonic pulse (5 MHz)	a	1043.8	5.6	0		0.3%	17.5
Difluoromethane (HFC-32) (CH_2F_2)	Takagi (1993)	saturated vapor pressure −35	−30–100	pulse echo (2 MHz)	b	532.7006	12.6824	0.2146	0.0005	0.4%	25
2,2-Dimethylpropane (C_5H_{12})	Lainez *et al.* (1990)	0.1–54	−10–160	pulse echo (3 MHz)	a	1014.5	8.4	0		0.05%	25
Dipropyl ether ($C_6H_{14}O$)	Pevnyi and Otpuschenikov (1980)	0.1–811	20–170	pulse echo (2 MHz)	a	1042.1	4.9	0		0.2%	30
Di-*iso*-propyl ether ($C_6H_{14}O$)	Pevnyi and Otpuschenikov (1980)	0.1–811	20–170	pulse echo (2 MHz)	a	1286.5	1.1	0		0.2%	20
1-Dodecanol ($C_{12}H_{26}O$)	Sysoev and Otpuschennikov (1979)	0.1–507	30–200	ultrasonic pulse (5 MHz)	a	1387.5	4.6	0		0.3%	30
Ethanol (C_2H_5OH)	Carnevale and Litovitz (1955)	0.1–196	30	pulse echo (45 MHz)	a	1114.3	6.0	0		0.2%	30
Ethanol (C_2H_5OH)	Hawley *et al.* (1970)	0.1–479	30	pulse echo (31 MHz region)	a	1133.5	5.1	0		0.3%	25
Ethanol (C_2H_5OH)	Brown *et al.* (1988)	0.1–6,800	25	Brillouin scattering	a	1139.5	2.0	0		0.3%	25
Ethanol (CH_3CH_2OH)	Bohidar (1989b)	0.1–82.5	20	Brillouin scattering		1210	3.3	2×10^{-3}		1%	20
Eugenol ($C_{10}H_{12}O_2$)	Hawley *et al.* (1970)	0.1–381	3	pulse echo (4.5 and 13.5 MHz regions)	a	1483.9	3.7	0		0.3%	30
n-Heptane (C_7H_{16})	Takagi (1978)	0.1–210	10–60	pulse echo (1 MHz)		1113.3	0.6749	-2.180×10^{-4}	3.8×10^{-8}	0.3%	30
n-Heptane (C_7H_{16})	Muringer *et al.* (1985)	0.1–263	−88–37	pulse echo (2 MHz)	a	1142.3	6.4	0		0.01%	25
1-Heptanol ($C_7H_{16}O$)	Sysoev and Otpuschennikov (1979)	0.1–811	15–180	ultrasonic pulse (5 MHz)	a	1327.1	4.2	0		0.3%	30
Hexane (C_6H_{14})	Bohidar (1988)	0.1–82.5	20	Brillouin scattering		1120	2.3	5×10^{-3}		1%	20
n-Hexane (C_6H_{14})	Hawley *et al.* (1970)	0.1–392	30	pulse echo (31.5 MHz)	a	1061.3	6.8	0		0.3%	30

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Liquid	Investigator(s)	Pressure (MPa)	Temp. range of original data (°C)	Experimental technique	Modeling technique	Coefficient				Uncertainty $< \pm x$	Temp. of data set (°C)
						a_0	a_1	a_2	a_3 (when available)		
n-Hexane (C$_6$H$_{14}$)	Allegra *et al.* (1970)	0.1–981	30	pulse echo (12 to 40 MHz)	a	1167.0	3.3	0		1%	30
n-Hexane (C$_6$H$_{14}$)	Takagi (1978)	0.1–210	10–60	ultrasonic pulse (1 MHz)		1062.1	0.7279	-2.519×10^{-4}	4.6×10^{-8}	0.3%	30
n-Hexane (C$_6$H$_{14}$)	Daridon *et al.* (1998)	0.1–150	20–100	pulse echo (3 MHz)		1054.2	8.3	0		0.09%	30
n-Hexanol (C$_6$H$_{14}$O)	Sysoev and Otpuschennikov (1979)	0.1–811	15–180	ultrasonic pulse (5 MHz)	a	1312.4	4.1	0		0.3%	30
Methanol (CH$_3$OH)	Carnevale and Litovitz (1955)	0.1–196	30	pulse echo (45 MHz)	a	1085.5	5.7	0		0.2%	30
Methanol (CH$_3$OH)	Hawley *et al.* (1970)	0.1–413	30	pulse echo (31 MHz region, 40.7 MHz)	a	1104.6	0.005	0		0.3%	30
Methanol (CH$_3$OH)	Brown *et al.* (1988)	0.1–6,800	25	Brillouin scattering	c	1264.4	1.3	0		0.3%	25
Methanol (CH$_3$OH)	Bohidar (1989b)	0.1–82.5	20	Brillouin scattering		1110	2.8	2×10^{-3}		1%	20
Methyl ethyl ketone (C$_4$H$_8$O)	Atoyan and Mamedov (1975)	0.1–162	0–200	pulse echo	a	1166.0	7.7	0		2.7%	20
Monochloropentafluoroethane (C$_2$ClF$_5$)	Takagi *et al.* (1989a)	0.1–51	10–100	pulse echo (2 MHz)	a	176.7232	21.7143	-0.4394	0.0038	2.4 m/s	30
Monochlorodifluoromethane (CHClF$_2$)	Takagi *et al.* (1989a)	0.1–51	10–100	pulse echo (2 MHz)	a	337.7989	19.0624	-0.3609	0.0031	2.4 m/s	30
Nitrobenzene (C$_6$H$_5$NO$_2$)	Takagi and Teranishi (1982b)	0.1–200 30	30 20–40	pulse echo (1 MHz)	a	1471.3	3.1	0		0.3%	20
Nitrobenzene (C$_6$H$_5$NO$_2$)	Takagi and Teranishi (1988)	0.1–100	25, 30	pulse echo (2 MHz)	a	1459.8	0.1	0		1.8 m/s	25
1-Nonanol (C$_9$H$_{20}$O)	Sysoev (1977)	0.1–101	20–200	pulse echo (5 MHz)	a	1350.4	4.8	0		0.3%	30
Octamethylcyclotetrasiloxane (C$_8$H$_{24}$O$_4$S$_{14}$)	Niepmann and Schmidt (1980)	coexistence line −60	27–177	pulse echo (2 MHz)	b	920.5811	5.9943	-0.0093	-0.0001	0.8 m/s	25
n-Octane (C$_8$H$_{18}$)	Takagi (1978)	0.1–210	10–60	pulse echo (1 MHz)		1155.8	0.6483	-2.141×10^{-4}	3.9×10^{-8}	0.3%	30
n-Octane (C$_8$H$_{18}$) +gaseous nitrogen (N$_2$)	Daridon *et al.* (1994)	0.1–100	30–100	pulse echo (3 MHz)	a	988.5781	8.1958	-0.0392	0.0001	0.25%	30
Pentafluoroethane (HFC-125) (CHF$_2$CF$_3$)	Takagi (1996)	saturation line −30	−30–60	pulse echo (2 MHz)	b	452.9293	8.3587	0.0940	0.0001	0.2%	25
Pentafluoropropyl alcohol (5FP)	Takagi and Naguchi (1992)	0.1–70	10–75	pulse echo (2 MHz)	b	759.6610	5.7122	-0.0335	0.0001	0.2%	25
n-Pentane (C$_5$H$_{12}$)	Belinskii and Ikvumov (1973)	0.1–784	20, 30, 40	ultrasonic pulse, (13 MHz)	a	1038.8	5.4	0		0.5%	30
n-Pentane (C$_5$H$_{12}$)	Lainez *et al.* (1990)	0.1–210	−10–160	pulse echo (3 MHz)		1038.8	5.4	0			
1-Pentanol (C$_5$H$_{12}$O)	Sysoev *et al.* (1976)	0.1–990	20.6, 150	ultrasonic pulse (5 MHz)	a	1302.1	3.9	0		0.3%	30
1-Pentanol (C$_5$H$_{12}$O)	Sysoev and Otpuschennikov (1979)	0.1–811	15–180	ultrasonic pulse (5 MHz)	a	1303.7	4.3	0		0.3%	20.6

TABLE 1. Coefficients of polynomial equations of form $c(p) = \sum_{i=0}^{4} a_i p^i$ for the organic liquids. Uncertainties are those noted by the original investigators for their experimental data. Under the 'Technique,' column, if no symbol is given, the original investigators (noted under 'Investigator(s)') calculated and published the a_i's in their own work, and the a_i's are simply presented here as originally calculated—Continued

Liquid	Investigator(s)	Pressure (MPa)	Temp. range of original data (°C)	Experimental technique	Modeling technique	Coefficient				Uncertainty $< \pm x$	Temp. of data set (°C)
						a_0	a_1	a_2	a_3 (when available)		
Polyethylsiloxane-3	Kagramanyan et al. (1978)	0.1–203	20–120	ultrasonic pulse (2.8 MHz)	c	1218.9	5.0	0		0.2%	20
Polyethylsiloxane-4,5	Kagramanyan et al. (1979)	0.1–203	30–100	ultrasonic pulse (2.8 MHz)	c	1228.7	5.2	0		0.2%	30
Polymethylsiloxane (PMS-1000)	Sysoev and Otpuschennikov (1979)	0.1–507	20–180	ultrasonic pulse (5 MHz)	a	1023.7	5.0	0		0.3%	20
Propane (C_3H_8)	Niepmann (1984)	coexistence line −60	−73–102	pulse echo (2 MHz)	b	705.7586	17.7558	−0.2511	0.0020	0.2%	25
1,3-Propanediol $(C_3H_8O_2)$	Sysoev and Otpuschennikov (1979)	0.1–861	19–180	ultrasonic pulse (5 MHz)	a	1616.6	2.6	0		0.3%	30
1-Propanol (C_3H_7OH)	Carnevale and Litovitz (1955)	0.1–196	30	pulse echo (25 MHz)	a	1189.3	5.5	0		0.2%	30
1-Propanol (C_3H_7OH)	Hawley et al. (1970)	0.1–493	23–75	pulse echo (22 and 31 MHz regions)	a	1208.4	5.0	0		0.3%	30
n-Propanol (C_3H_7OH)	Bohidar (1989b)	0.1–82.5	20	Brillouin scattering		990	3.2	3×10^{-3}		1%	20
Tetraethoxysilane	Takagi et al. (1989b)	0.1–100	10–60	pulse echo (2 MHz)	a	1056.7	6.0	0		0.3%	25
Tetraethylsilane	Takagi et al. (1989b)	0.1–100	10–60	pulse echo (2 MHz)	a	1203.9	6.4	0		0.3%	25
1,1,1,2-Tetrafluoroethane (HFC-134a) (CF_3CH_2F)	Guedes and Zollweg (1992)	saturation line −70	−94–107	pulse echo (3 MHz)	a	471.2701	7.3560	0.0527	−0.0011	0.05%	27
Tetrafluoro-propyl alcohol (4FP)	Takagi and Naguchi (1992)	0.1–70	10–75	pulse echo (2 MHz)	b	989.3100	4.1548	−0.0165	0.0001	0.2%	25
Tetramethylsilane	Takagi et al. (1989b)	0.1–200	10–60	pulse echo (2 MHz)	a	852.1915	8.8248	−0.0372	0.0001	0.3%	25
Toluene (C_7H_8)	Hawley et al. (1970)	0.1–522	30, 75	pulse echo (22.5 MHz region)	a	1288.5	4.6	0		0.3%	30
Toluene (C_7H_8)	Allegra et al. (1970)	0.1–981	30	pulse echo (12–40 MHz)	a	1327.1	3.7	0		1%	30
Toluene (C_7H_8)	Muringer et al. (1985)	0.1–263	−100–47	pulse echo (2 MHz)	a	1314.3	3.9	0		0.01%	25
Toluene (C_7H_8)	Takagi and Teranishi (1985)	0.1–180	30	ultrasonic pulse (1 MHz)	a	1286.0	4.9	0		0.3%	30
Toluene (C_7H_8)	Bohidar (1989b)	0.1–82.5	20	Brillouin scattering		1360	3.2	1×10^{-3}		1%	20
Trichlorofluoromethane (CFC-11) $(CFCl_3)$	Lainez et al. (1989)	0.1–210	80–140	pulse echo (3 MHz)	a	577.3518	5.9918	−0.0228		0.05%	80
Trichlorofluoromethane (CFC-11) $(CFCl_3)$	Takagi (1991)	0.1–75	10–100	pulse echo (2 MHz)	b	693.2871	6.4504	−0.5045	0.0003	0.2%	25
Trichloromethane $(CHCl_3)$	Takagi (1994)	0.1–50	25–80	pulse echo (2 MHz)	b	742.8647	5.6065	−0.0367	0.0002	0.2%	25
Trifluoroethyl alcohol (3FE)	Takagi and Naguchi (1992)	0.1–70	10–75	pulse echo (2 MHz)	a	985.2863	4.0784	−0.0166		0.2%	25
1-Undecanol $(C_{11}H_{24}O)$	Sysoev (1977)	0.1–101	20–200	pulse echo (5 MHz)	a	1375.1	5.2	0		0.3%	30

TABLE 1. Coefficients of polynomial equations of form $c(p) = \sum_{i=0}^{4} a_i p^i$ for the organic liquids. Uncertainties are those noted by the original investigators for their experimental data. Under the 'Technique,' column, if no symbol is given, the original investigators (noted under 'Investigator(s)) calculated and published the a_i's in their own work, and the a_i's are simply presented here as originally calculated—Continued

Liquid	Investigator(s)	Pressure (MPa)	Temp. range of original data (°C)	Experimental technique	Modeling technique	a_0	a_1	a_2	a_3 (when available)	Uncertainty $< \pm x$	Temp. of data set (°C)
o-Xylene $(C_6H_4(CH_3)_2)$	Takagi and Teranishi (1985)	0.1–180	30	ultrasonic pulse (1 MHz)	a	1327.6	5.0	0		0.3%	30

[a]The authors of this paper performed the calculations necessary to find the a_i using data supplied by the original investigator(s).
[b]Coefficients a_i were obtained by taking double sum coefficients of the form $c = \sum_{i=0}^{n}\sum_{j=0}^{m} a_{ij}T^i p^j$, which were supplied by the original investigators, projecting the data set from those given coefficients, and pulling new single sum coefficients of the form $c(p) = \sum_{i=0}^{4} a_i p^i$ at the specified temperature.
[c]The authors performed the calculations necessary to find the a_i using data supplied by the investigator, but the resulting polynomial produced by MATLAB was badly conditioned.

under pressurized conditions, notwithstanding the difference in pressure ranges for which the coefficients were calculated. Even third order polynomials showed these discrepancies—carbon tetrachloride, for example, had an a_1 coefficient of 12.2643 given by Lainez *et al.* (1987), while Bobik *et al.* (1979) showed an a_1 of 4.0175. a_2 coefficients were -0.0258 and -0.0164. The difference between results ascertained via ultrasound versus Brillouin scattering is also sometimes striking. For example, ethanol was found to have a_1 coefficients of 5.1, 2.0, and 3.3 by Hawley *et al.* (1970), Brown *et al.* (1988), and Bohidar (1989b), respectively, the later two of whom used Brillouin scattering.

It is worthwhile to explore how adding more coefficients to the polynomial used to fit the data set reduces error, and to see how error can also be affected by the number of independent parameters such as pressure *and* temperature, as opposed to just pressure, the equation was being made to fit. We used multiple polynomial regression curve fitting with MATLAB to analyze the 118 experimental results from Lainez (1989) for trichlorofluoromethane for temperatures between 353 and 413 K and pressures between 0 and 210 MPa (gauge). Listing 1 shows the MATLAB code to generate the coefficients a_i (or a_{ij}) through least-squares analysis of the experimental data, as well as to compute the outputs and errors. Listing 2 is the MATLAB code for our first degree polynomial double sum.

Listing 1: MATLAB code to generate the coefficients a_i (or a_{ij}) through least-squares analysis of the experimental data

```
—polynomial function 'POL1'
function o=POL1(beta, x)
  b1=beta(1); b2=beta(2); b3=beta(3); b4=beta(4);
  o=b1+b2.* (x(:,1)-380)+b3.* (x(:,2)-100)+b4.*
  (x(:,2)-100).* (x(:,1)-380);
```

TABLE 2. Difference between coefficients for a second versus third degree polynomial calculated from the same set of data [Lainez *et al.* (1987), carbon tetrachloride]

	a_0	a_1	a_2	a_3
2nd degree polynomial	824.9840	15.9333	-0.1130	N/A
3rd degree polynomial	848.6372	12.2643	-0.0258	-0.0005

Listing 2: MATLAB code for first degree polynomial double sum

```
TP=[T'P'];
beta=[0 0 0 0];
beta=beta';
[betahat, resid, J]=nlinfit(TP, C, 'POL1', beta);
[yhat, delta]=nlpredci('POL1', TP, betahat, resid, J);
disp('First Order');
betahat
opd=[C' yhat delta]
err=mean(abs((delta)./C'))*100;
```

The various polynomials fitted to these data are shown in Table 3. It is clear from the table that each additional term on the *single* series polynomial reduces the average fractional error between modeled results and experimental results by roughly two thirds. For the double series polynomial, which is dependent on both temperature and pressure, each additional set of terms (for example, increasing the number of terms summed from $\sum_{i=0}^{1}\sum_{j=0}^{1}$ to $\sum_{i=0}^{2}\sum_{j=0}^{2}$) reduces the error by a little more than one half. The error from Lainez's fractional polynomial is indeed smaller, although more difficult to calculate and fit. However, we point out that using higher polynomials to describe the data may introduce oscillations due to the curve fitting that may reduce accuracy.

5. Conclusions

Creation of a common, similar library of polynomial equations to describe the results of the wide variety of speed of sound experiments has revealed unexpected discrepancies in data, in many cases beyond what would be expected from experimental uncertainty, differing pressure ranges, and small differences in temperature. It is clear that the results of some experimental apparatus under high pressure conditions are not reliable. Notwithstanding these surprises, it is felt that having a large library of descriptive polynomials will enhance the ability of future investigators to explore differences in speed of sound as a function of pressure for a variety of purposes. It may be of interest to apply the method of response surfaces [Box and Draper (1997)] to try and identify which of the 16 parameters (a_i) in the fractional polynomial (footnote b of Table 3) are actually redundant and

TABLE 3. Absolute average fractional error observed in speed of sound as a function of pressure. These calculations were performed for pressure data between 0 and 210 MPa (gauge) obtained for experimentally obtained speed of sound data in trichlorofluoromethane at 80 °C [Lainez *et al.* (1989)] as a function of degree and type of polynomial and number of independent parameters

Polynomial	Absolute average fractional error [a]
$c(p)=\sum_{i=0}^{1} a_i p^i$	2.54
$c(p)=\sum_{i=0}^{2} a_i p^i$	0.71
$c(p)=\sum_{i=0}^{3} a_i p^i$	0.25
$c(p)=\sum_{i=0}^{4} a_i p^i$	0.0991
$c(p,T)=\sum_{i=0}^{1}\sum_{j=0}^{1} a_{i,j}(p-p_0)^i(T-T_0)^j$	1.106
$c(p,T)=\sum_{i=0}^{2}\sum_{j=0}^{2} a_{i,j}(p-p_0)^i(T-T_0)^j$	0.4475
$c(p,T)=\sum_{i=0}^{3}\sum_{j=0}^{3} a_{i,j}(p-p_0)^i(T-T_0)^j$	0.2161
$c(p,T)=\sum_{i=0}^{4}\sum_{j=0}^{3} a_{i,j}(p-p_0)^i(T-T_0)^j$	0.0937
$c(p,T)=\sum_{i=0}^{3}\sum_{j=0}^{4} a_{i,j}(p-p_0)^i(T-T_0)^j$	0.401
$c(p,T)=\dfrac{\sum_{i=0}^{2}\sum_{j=0}^{1}a_{i,j}(p-p_0)^i(T-T_0)^j}{\sum_{k=0}^{2}\sum_{l=0}^{2}b_{k,l}(p-p_0)^k(T-T_0)^l}$ [b]	0.040 (.0873%)

[a]Absolute average fractional error $=(100\times\Sigma_i|c_i-c_{(\text{calc})i}/c_i|)(1/i)$.
[b]Lainez's calculated coefficients, as cited in Lainez *et al.* (1989), were used for this equation. The corresponding fractional error as calculated by Lainez is given.

may be omitted. Finally, it is seen that although there are many experimental results, an underlying theory still lies in the future.

6. List of Terms

$$\beta=\frac{1}{v}\left(\frac{\partial v}{\partial t}\right)_P=-\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P=\text{coefficient of thermal expansion,}$$

$$\kappa_T=-\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T=\frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right)_T=\text{isothermal compressibility factor,}$$

$$\kappa_S=-\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_S=\frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right)_S=\text{adiabatic compressibility factor (bulk modulus for adiabatic compression),}$$

ρ = density,
γ = C_P/C_V,
C_P = specific heat at constant pressure, and
C_V = specific heat at constant volume.

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