60 *J. Chem. Eng. Data* **1993,** *38,* 60–62

Ultrasonic Speeds in Liquid 1,1-Dichloro-1-fluoroethane at Temperatures from 283 to 373 K and Pressures up to 50 MPa

Toshiharu Takagi* and Masaru Hongo†

Faculty of Engineering and Design, Kyoto Institute of Technology, Matsugasaki, Sakyoku, Kyoto 606, Japan, and College of Industrial Technology, Nihon University, Narashinoshi, Chiba 275, Japan

The ultrasonic speeds, *u*, in the liquid phase of 1,1-dichloro-1-fluoroethane, CCl_2FCH_3, were measured along 11 isotherms from 283 to 373.15 K and from 0.1 MPa or near the vapor pressure to about 50 MPa. The measurements were carried out by a sing-around technique operated at a frequency of 2 MHz with an uncertainty of less than ±0.2%. The ultrasonic speeds and related thermodynamic properties for CCl_2FCH_3 appear to have characteristics different from those for CCl_3F and $CHCl_2CF_3$ reported elsewhere.

Introduction

In earlier papers, we reported the ultrasonic speeds in liquid 1,1-dichloro-2,2,2-trifluoroethane, $CHCl_2CF_3$ (HCFC-123) (*1*), and 1,2-dichloro-1,2,2-trifluoroethane, $CHClFCClF_2$, (HCFC-123a) (*2*). These fluids were recommended as new ozone-safe compounds suitable for replacing trichlorofluoromethane, CCl_3F (CFC-11), and were chiefly used as polymer solvents and blowing agents. In previous studies, we found that these ethane-based compounds show significant differences in the observed ultrasonic speeds and thermodynamic properties compared with CCl_3F, especially in the high-temperature region.

1,1-Dichloro-1-fluoroethane, CCl_2FCH_3 (HCFC-141b), is also expected to be a suitable replacement for CCl_3F. However, few measurements on the thermophysical properties have been reported by Chae et al. (*3*), Weber (*4*), and Maezawa et al. (*5*). Polymers are soluble in these compounds to an extent similar to that for CCl_3F. In our previous work, a fluorine-containing rubber O-ring or Teflon-coated O-ring was used as a piston seal in the sample–oil separator to protect the O-ring from the sample fluids. But, the barrier for the O-ring leaked between the sample and the oil during the experiment. This was caused by the high solubility of polymer or the inflexibility resulting from the Teflon coating. In the present work, the acoustic interferometer was modified to correct this problem. The ultrasonic speed in liquid CCl_2FCH_3 was measured at various temperatures and pressures, and the results were compared with those for CCl_3F and $CHCl_2CF_3$ reported in our previous papers.

Experimental Section

The method used to measure the ultrasonic speeds was a sing-around technique operated at a frequency of 2 MHz, similar to that outlined previously (*1, 2*). Figure 1 shows a new fixed-path acoustic interferometer employing a Teflon capsule modified from that used in our previous work (*6*). The sample chamber was designed to control freely the inner volume by the strain of the Teflon capsule from about 45 to 35 cm³ because these fluorocarbon fluids have a large expansibility and compressibility.

An interferometer placed in the high-pressure vessel was immersed in a liquid bath controlled to within ±0.02 K from 283 to 343 K and ±0.03 K from 353 to 373 K. The pressure, generated using a silicon oil of viscosity 50 mPa·s, was measured by three strain gauges with ranges of 10, 30, and 70 MPa to within ±0.03, ±0.05, and ±0.08 MPa, respectively.

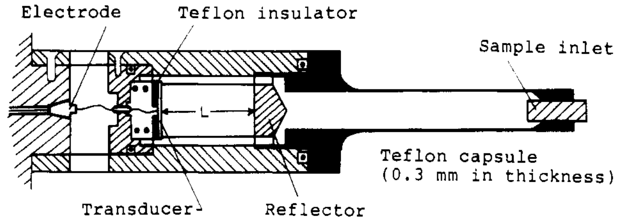

Figure 1. Acoustic interferometer.

Table I. Physical Properties for Each Compound

	CCl_3F^a	$CHCl_2CF_3^b$	$CCl_2FCH_3^c$
MW	137.36	152.93	116.95
T_b	296.9	300.84	305.26
	Critical Constants		
T_c/K	471.2	456.86	477.35
p_c/MPa	4.14	3.666	4.25
ρ_c/(kg·m^{-3})	554	555	461
	At 298.15 K and Saturated Liquid		
ρ/(kg·m^{-3})	1476.0	1462.2	1229.0
V_m/(cm^3·mol^{-1})	93.06	104.02	95.15
L_f^e/pm	8.0	10.9	9.4
p_s/kPa	105.6	91.8	79.0
μ^d/(10^{30} C·m)	1.50	4.523	6.717

[a] Reference 8. [b] Reference 9. [c] Reference 5. [d] Reference 10. [e] L_f is the intermolecular free length.

The acoustic path length *L* (=25.123 mm) was determined by using the ultrasonic speed in pure tetrachloromethane, CCl_4, 921.11 ± 0.07 m·s^{-1} at 298.15 K and 0.1 MPa measured accurately by Tamura et al. (*7*). The influence of *L* due to the temperature and pressure changes was calibrated from the expansivity and compressibility of the metal. The probable uncertainty in the measurements of *u* is ±0.2%, except for values in the vicinity of the saturated vapor states at high temperatures.

1,1-Dichloro-1-fluoroethane, CCl_2FCH_3, was supplied by Daikin Industrials Ltd.; its purity, determined by GLC, was better than 98.9 mol %. The physical properties are listed in Table I with those for CCl_3F and $CHCl_2CF_3$.

Results and Discussion

The experimental results of the ultrasonic speeds, *u*, in the liquid phase of CCl_2FCH_3 at pressure *p* are listed in Table II. For this compound, no experimental study on the *u* value has been reported previously. To confirm the reliability of

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* To whom correspondence should be addressed at the Kyoto Institute of Technology.
† Nihon University.

0021-9568/93/1738-0060$04.00/0

Table II. Ultrasonic Speed, u, in the Liquid Phase of 1,1-Dichloro-1-fluoroethane, CCl_2FCH_3, at Various Temperatures, T, and Pressures, p

p/MPa	u/(m·s^{-1})	p/MPa	u/(m·s^{-1})	p/MPa	u/(m·s^{-1})	p/MPa	u/(m·s^{-1})	p/MPa	u/(m·s^{-1})
283.15 K									
0.045[a]	877.7[b]	4.860	903.9	12.46	941.7	23.15	989.1	40.31	1055.3
0.1	878.4	5.735	908.5	15.16	954.1	25.74	999.7	45.23	1072.8
2.118	889.5	7.313	916.6	17.51	964.7	30.42	1018.4	50.17	1089.8
3.081	894.6	9.82	929.1	20.01	975.7	35.11	1036.1		
293.15 K									
0.066[a]	840.6[b]	5.762	873.2	12.43	907.4	23.21	957.3	40.32	1026.2
0.1	841.2	6.447	876.8	15.06	920.3	25.73	968.0	45.21	1044.1
2.291	853.4	7.821	884.1	17.80	932.9	30.56	988.2	50.01	1061.2
4.673	867.4	9.98	895.2	20.37	944.7	34.96	1006.1		
298.15 K									
0.079[a]	821.0[b]	4.896	849.7	11.13	883.2	20.64	929.4	40.19	1011.2
0.1	821.9	5.984	855.8	12.86	892.0	25.16	949.7	44.71	1028.3
2.954	838.6	7.748	865.4	15.06	902.8	30.24	971.6	49.89	1047.2
4.111	845.4	9.43	874.3	17.41	914.2	35.00	990.9		
303.15 K									
0.094[a]	803.5[b]	5.727	836.6	13.14	878.0	22.69	923.9	39.78	995.5
0.1	803.5	7.748	847.7	15.16	888.2	25.58	936.8	45.15	1016.1
2.668	819.0	9.302	856.3	17.61	900.0	30.93	960.5	50.01	1034.5
3.772	825.5	11.21	866.6	20.07	911.7	35.15	977.2		
313.15 K									
0.131[a]	766.6[b]	5.314	800.1	13.14	845.6	24.40	902.4	39.60	968.1
0.640	769.8	7.061	810.8	15.39	857.7	25.57	907.6	43.66	984.2
1.499	775.5	9.28	824.0	17.48	868.4	29.91	927.3	49.34	1006.1
3.739	790.2	11.30	835.5	20.17	881.9	34.68	948.2		
323.15 K									
0.180[a]	729.7[b]	4.517	760.2	12.36	809.8	26.17	882.5	41.75	950.8
0.632	732.9	6.920	776.2	16.88	835.2	31.51	907.2	46.46	970.0
2.398	746.0	9.014	789.4	21.16	857.7	36.51	929.2	52.01	991.2
333.15 K									
0.241[a]	693.1[b]	6.251	737.4	16.46	801.9	31.02	877.2	45.24	939.6
0.729	696.6	8.448	752.7	20.70	825.6	35.85	899.4	51.16	962.6
3.480	718.0	11.60	773.0	26.63	856.1	40.94	921.6		
343.15 K									
0.319[a]	656.6[b]	7.166	710.2	16.91	774.8	31.49	853.1	46.50	920.6
2.388	673.9	8.828	722.6	21.67	802.2	36.05	874.7	51.26	940.1
4.882	693.6	12.08	745.5	26.78	829.7	41.47	899.1		
353.15 K									
0.414[a]	620.4[b]	6.967	676.0	16.53	743.9	30.88	824.6	45.42	982.5
2.039	635.2	9.503	695.9	21.31	772.7	35.96	849.6	51.14	916.8
4.596	657.5	12.02	713.9	25.86	798.3	40.54	870.9		
363.15 K									
0.531[a]	584.4[b]	7.091	644.0	16.16	711.7	31.31	800.9	46.07	871.9
3.022	607.6	9.345	662.3	21.31	744.7	36.25	826.1	50.75	892.1
4.582	622.1	12.08	683.1	26.67	775.7	41.27	850.0		
373.15 K									
0.671[a]	549.2[b]	7.203	611.1	16.17	683.4	30.85	774.4	46.44	851.8
2.774	568.9	9.329	629.5	20.97	715.9	35.15	797.4	50.42	869.6
4.996	590.4	12.37	654.3	25.89	746.5	41.15	827.2		

[a] Vapor pressure, p_s. [b] Estimated ultrasonic speed at p_s.

the apparatus, we made measurements on u in CCl_3F at 353.15 K at 5 and 40 MPa. The measured values obtained were 952.2 and 788.4 m·s^{-1}, respectively. These values are in agreement within ±0.16% with those reported by Lainez et al. (*11*). The ultrasonic speeds obtained for the present fluid are presented graphically in Figure 2. These values have been represented by the following polynomial equation:

$$u/(\mathrm{m{\cdot}s^{-1}}) = \sum_{i=0}^{2}\sum_{j=0}^{3} a_{ij}t^{i}(p/\mathrm{MPa})^{j} \qquad (1)$$

where t is T/K − 298.15. The values of the coefficients a_{ij}, calculated by a least-squares analysis using all the experimental data weighted equally, are listed in Table III with the standard deviation from eq 1. The maximum deviations of observed values from the equation occurred chiefly in the vicinity of the vapor pressure in the high-temperature region.

The measurement of ultrasonic speeds was carried out at narrow pressure intervals at the vapor pressure, p_s, where the values were strongly dependent on pressure. From the coefficients in Table III, the ultrasonic speed, u_{p_s}, for p_s was calculated by extrapolation to the vapor pressure. These values are listed in Table II with the vapor pressure derived from the equation reported in ref 5. The experimental error of u_{p_s} values increased with increasing temperature. The results of u_{p_s} for the saturated liquid in CCl_2FCH_3 are plotted in Figure 3 as a function of temperature together with those for CCl_3F and $CHCl_2CF_3$ reported in our previous papers (*1*). From the extrapolated values of u_{p_s}, the isentropic compressibility, κ_S [$=(\rho u^2)^{-1}$], for $CHCl_2CH_3$ was estimated at the saturated pressure, and the values are also plotted in Figure 4 with those for other methane and ethane refrigerants. The saturated liquid density, ρ, used in this estimation was derived from the equation given in ref 5.

Table III. Coefficients a_{ij} of Equation 1[a]

i	$j = 0$	$j = 1$	$j = 2$	$j = 3$
0	8.21763×10^{2}	-3.71964	-1.22580×10^{-4}	6.02793
1	4.01296×10^{-2}	2.56337×10^{-4}	-4.20218×10^{-2}	-6.03081×10^{-4}
2	-5.94540×10^{-6}	2.38331×10^{-4}	4.34545×10^{-6}	4.70248×10^{-8}

[a] The standard deviation $\delta_{std} = 0.0536$. $\delta_{std} = \sum|100(u_{exptl} - u_{calcd})/u_{calcd}|/n$, where n is the number of experimental points.

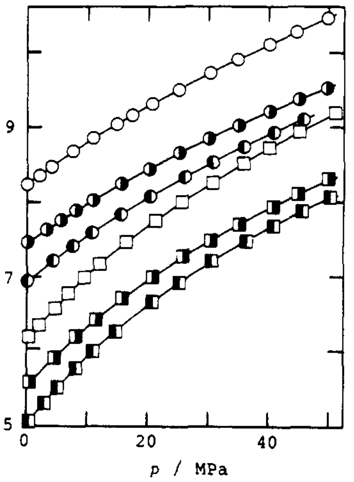

Figure 2. Pressure, p, dependence of ultrasonic sound, u: ○, ◑, ◐, 298.15 K; □, ◨, ◧, 353.15 K; ○, □, CCl_2FCH_3 (this work); ◑, ◨, CCl_3F (ref 1); ◐, ◧, $CHCl_2CF_3$ (ref 1).

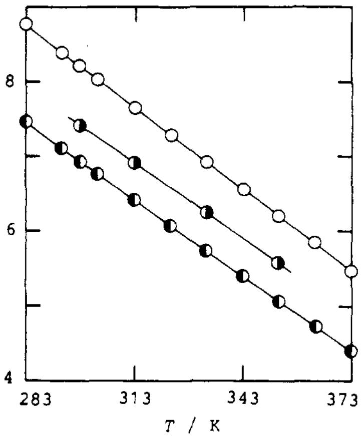

Figure 3. Temperature, T, dependence of ultrasonic speed, u, at the saturated liquid condition: ○, CCl_2FCH_3 (this work); ◑, CCl_3F (ref 1); ◐, $CHCl_2CF_3$ (ref 1).

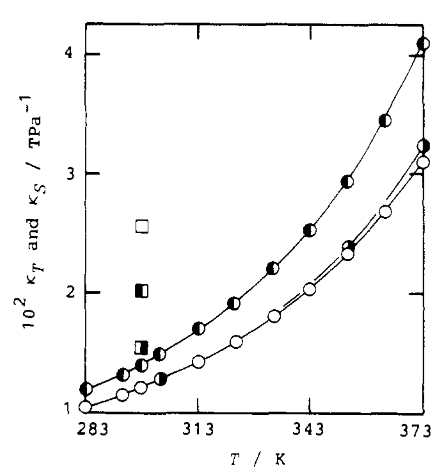

Figure 4. Temperature, T, dependence of isentropic, κ_S, and isothermal, κ_T, compressibilities at the saturated liquid condition: ○, ◑, ◐, κ_S; □, ◨, ◧, κ_T; ○, □, CCl_2FCH_3 (this work); ◑, ◨, CCl_3F (ref 1); ◐, ◧, $CHCl_2CF_3$ (ref 1).

As can be seen in these figures, the ultrasonic speeds, u, for CCl_2FCH_3 differ considerably from those of the other two compounds. For the hydro- and/or chlorofluorocarbons measured previously, the value of u can be discussed qualitatively by the differences in molecular structure on the basis of Eyring's intermolecular free volume theory (*6, 12*). According to this model, the acoustic signal, excited in the sample for the u measurement, is transferred in accordance with the different characteristics in the space of two neighboring molecules for different compounds. In general, a simple fluid such as CCl_4 has a small intermolecular free length, L_f, and shows a large u. Now, assuming that these sample fluids consist of spherical molecules, the values of L_f estimated at 298.15 K and p_s increase in the order CCl_3F < CCl_2FCH_3 < $CHCl_2CF_3$ as listed in Table I. However, in CCl_2FCH_3, the ultrasonic speed observed is larger than that for the simple fluid CCl_3F in the whole experimental region. This implies that CCl_2FCH_3 has a thermodynamic element different from those of the other two fluids; therefore, the u results cannot be explained relatively only by the magnitude of L_f.

Among the compounds studied previously, $CHCl_2CF_3$ has a larger value of κ_S compared with that for CCl_3F, but the κ_S values for CCl_2FCH_3 estimated here are parallel to those of CCl_3F as shown in Figure 4. The isothermal compressibility, κ_T, for CCl_2FCH_3, estimated at 298.15 K and p_s from the *PVT* properties reported elsewhere, has a notably larger value compared with those for the other two compounds. That is, for CCl_2FCH_3 the ratio of heat capacities, γ [$= C_p/C_v = \kappa_T/\kappa_S$], is large, and the γ values decrease in the order CCl_2FCH_3 > $CHCl_2CF_3$ > CCl_3FF. Furthermore, this order correlates with the dipole moment, which is determined by the difference of the bond energy of C–F and C–H in the various molecules. Although the three fluids have nearly the same physical properties as listed in Table I, the differences in the ultrasonic speeds and related thermodynamic properties appear to be a result of different interactions.

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Received for review March 17, 1992. Revised July 22, 1992. Accepted September 10, 1992.