Speed of Sound in Liquid 1,2-Dichloro-1,2,2-trifluoroethane from 283 to 373 K and to 75 MPa

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The speed of sound in liquid 1,2-dichloro-1,2,2-trifluoroethane, $CHClFCClF_2$, was measured from 283 to 373 K and from 0.1 MPa or near the saturation pressure to about 75 MPa by a sing-around technique operated at a frequency of 2 MHz. The estimated uncertainty of the measurement is ±0.2%. The vapor pressures were measured by a static method from 323 to 368 K with an uncertainty of ±0.3%. These results were used to calculate the speed of sound along the saturation boundary. The variations of the speed of sound with temperature and pressure are discussed by comparing the results with previous results for 1,1-dichloro-2,2,2-trifluoroethane, $CHCl_2CF_3$.

Introduction

1,1-Dichloro-2,2,2-trifluoroethane, $CHCl_2CF_3$ (HCFC-123), is recommended as an environmentally acceptable alternative to trichlorofluoromethane, CCl_3F (CFC-11), because both fluids have similar properties such as critical constants and saturated gas and liquid densities (*1*, *2*). In a previous paper (*3*), large differences in the speed of sound and related properties for these two substances, especially at higher temperatures, were noted. 1,2-Dichloro-1,2,2-trifluoroethane, $CHClFCClF_2$ (HCFC-123a), an isomer of $CHCl_2CF_3$, is also preferred as a replacement of CCl_3F. There have been few measurements on the thermodynamic properties of $CHClFCClF_2$. In this paper, we report new experimental values of the speed of sound at temperatures from 283 to 373 K and pressures below 75 MPa and calculated values along the saturated curve at temperatures from 283 to 373 K for $CHClFCClF_2$ (HCFC-123a). The temperature and pressure effects on the speed of sound for $CHClFCClF_2$ resulting from the molecular structure are discussed together with the results for $CHCl_2CF_3$.

Experimental Section

Materials. 1,2-Dichloro-1,2,2-trifluoroethane, $CHClFCClF_2$, was research grade material supplied by Daikin Industrials Ltd. The sample purity, determined by GLC, was better than 99.8 wt %. The physical properties are listed in Table I together with those of CCl_3F and $CHCl_2CF_3$.

Measurements. The method employed for the measurement of speed of sound u was a sing-around technique operated at a frequency of 2 MHz, similar to that described previously (*3*). The temperature of the thermostat was kept within ±0.02 K from 283 to 343 K and ±0.03 K from 353 to 373 K. The temperature was measured by means of a digital thermometer with a quartz sensor, which has a precision of ±0.01 K. The pressure was measured by two strain gauges of 10- and 100-MPa maximum pressure, and their uncertainties were estimated to be no greater than ±0.03 and ±0.08 MPa, respectively. The estimated instrumental uncertainty was within ±0.2%, as determined from previous measurements on the speed of sound u of CCl_4 and CCl_3F (**3**). The values of u for $CHClFCClF_2$ determined at 298.15 and 353.15 K were reproducible to ±0.4 $m \cdot s^{-1}$, corresponding to ±0.1%, as determined from duplicate runs.

The vapor pressure of $CHClFCClF_2$ was measured from 323 to 368 K by a static method, employing a sample vessel of 46 cm^3, with the uncertainty of ±0.3% using a method described elsewhere (*8*).

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Table I. Physical Properties

chemical formula	CCl_3F	$CHCl_2CF_3$	$CHClFCClF_2$
molecular weight	137.37	152.93	152.93
melting temperature/K	162.15	166.15	195.1
boiling temperature/K	296.90	300.25	301.15
critical constants			
T_c/K	471.20[a]	456.86[b]	461.70,[c] 458.35[d]
P_c/MPa	4.41[a]	3.67[b]	3.99,[c] 4.47[d]
$\rho_c/(kg \cdot m^{-3})$	554[a]	550[b]	541,[c] 625[d]
parameters at 298.15 K and 0.1 MPa			
$\rho/(kg \cdot m^{-3})$	1494[e]	1475[d]	1482.3[f]
n_D[g]	1.3865	1.3282	1.3304
dipole moment, $\mu/(10^{-30}$ C·m)	0.45[a]	0.8[h]	

[a] Reference 4. [b] Reference 5. [c] Reference 6. [d] Reference 7. [e] Reference 4, at 290.35 K. [f] Measured by a Ostwald pycnometer. [g] Measured by an Abbe refractometer. [h] Reference 3, estimated by a Debye equation from dielectric constant data.

Results and Discussion

The experimental results for the speed of sound in liquid $CHClFCClF_2$ at various pressures p are summarized in Table II. Six isotherms are illustrated in Figure 1. They show that u is a smoothly varying function of p. The temperature dependence for selected isotherms is shown in Figure 2. The results can be represented as a function of temperature and pressure by the following polynomial equation:

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

where $t = T/K - 298.15$. The values of the coefficient a_{ij} were calculated from the method of least-squares using all experimental data weighted equally and are listed in Table III. The maximum and standard deviations of the experimental results from the above equation are 0.3 and 0.02%, respectively.

For refrigerants, the saturated vapor pressure is an important property. In this work, the vapor pressures p_s for $CHClFCClF_2$ were measured by a static method. The speed of sound u_{p_s} for the saturated liquid was estimated by the extrapolation of the data at high pressure to p_s using the coefficients a_{ij} in eq 1. The values of p_s and u_{p_s}, obtained are also listed in Table II. The vapor pressure was measured with a precision of ±1 kPa, by a dead-weight pressure balance whose lower limit of detection was about 0.2 MPa. In the range of temperatures from 283.15 to 323.15 K, the values of p_s given in Table II were derived from Mears's equation reported by Ootake et al. (*6*). The literature values at higher temperatures are slightly higher, by about 0.01 MPa, compared with the present values,

Table II. Speed of Sound $u/(\mathrm{m \cdot s^{-1}})$ for Liquid 1,2-Dichloro-1,2,2-trifluoroethane at Several Pressures p/MPa[a]

p/MPa	$u/(\mathrm{m \cdot s^{-1}})$	p/MPa	$u/(\mathrm{m \cdot s^{-1}})$	p/MPa	$u/(\mathrm{m \cdot s^{-1}})$	p/MPa	$u/(\mathrm{m \cdot s^{-1}})$	p/MPa	$u/(\mathrm{m \cdot s^{-1}})$
				283.15 K					
0.056*	758.6**	7.501	797.5	24.45	874.5	42.50	943.0	62.36	1007.5
0.100	759.4	11.56	817.6	28.25	889.9	46.70	957.5	67.51	1023.1
1.899	768.7	15.93	837.8	32.50	906.3	52.28	976.2	74.99	1043.4
5.110	785.2	20.88	859.4	36.23	920.4	56.48	989.0	75.00	1048.8
				293.15 K					
0.074*	722.9**	8.93	771.2	25.98	850.8	46.97	931.1	66.18	994.1
0.100	723.7	13.33	793.5	31.77	874.5	50.79	944.2	72.23	1012.2
4.062	744.6	17.11	811.6	36.09	891.4	57.43	966.3	76.57	1025.2
6.993	760.8	21.30	830.7	41.23	910.6	61.87	980.6		
				298.15 K					
0.089*	705.0**	9.18	755.3	26.18	836.7	45.69	912.9	65.47	979.2
0.100	705.1	11.78	769.0	31.51	859.2	50.93	931.2	70.01	993.1
3.882	726.4	16.75	793.7	35.87	876.5	55.46	946.7	75.12	1009.0
6.714	742.3	21.35	815.4	41.31	897.2	60.87	964.5		
				303.15 K					
0.106*	687.2**	8.78	737.5	26.03	822.2	46.09	901.9	65.73	968.3
0.585	689.8	11.86	754.2	30.77	842.3	49.98	915.8	70.01	981.8
4.233	711.4	16.38	777.4	36.16	864.3	56.11	937.0	75.81	999.3
6.873	726.6	20.82	798.7	41.31	884.2	61.31	954.1		
				313.15 K					
0.149*	651.6**	8.32	702.6	26.13	795.0	46.26	878.8	66.08	947.5
0.530	653.7	11.30	719.6	31.62	819.1	51.40	897.5	70.19	960.7
3.313	672.1	16.07	746.2	36.32	839.8	56.07	914.0	75.07	975.0
6.275	690.2	21.08	771.3	40.26	878.8	60.93	929.6		
				323.15 K					
0.204*	616.2**	8.86	674.3	26.25	768.3	45.75	851.2	65.55	922.2
0.699	617.7	11.68	691.5	31.20	791.1	50.87	870.8	70.31	937.2
4.198	643.4	15.74	714.8	35.83	811.2	56.09	889.6	75.54	954.2
6.731	660.6	21.28	744.0	41.23	833.4	60.62	905.6		
				333.15 K					
0.263*	580.9**	8.50	640.3	21.34	717.6	40.98	809.0	60.93	885.0
0.740	583.8	11.23	657.8	26.08	741.7	45.97	829.4	65.53	901.3
3.490	604.3	15.71	685.1	31.43	767.2	51.42	850.6	70.29	917.1
6.035	623.2	16.41	689.4	36.39	789.5	56.11	867.3	75.47	933.5
				343.15 K					
0.349*	545.9**	8.97	613.8	26.63	719.0	45.55	805.1	65.34	880.0
0.852	548.5	11.82	633.3	31.05	740.8	51.18	827.6	70.23	896.5
3.992	575.8	15.94	659.6	36.10	764.4	55.52	844.2	75.48	914.0
6.969	599.1	21.44	691.4	41.13	786.5	60.72	863.5		
				353.15 K					
0.454*	511.2**	9.86	587.8	26.77	695.3	46.70	787.9	66.41	862.6
0.914	514.7	12.98	610.5	31.59	720.0	51.42	807.5	70.97	879.5
4.373	545.1	16.83	636.2	36.80	744.8	56.70	827.2	76.42	898.5
7.058	567.5	22.12	669.3	41.35	765.4	61.85	846.3		
				363.15 K					
0.581*	476.8**	9.37	554.4	26.42	668.7	47.17	768.4	65.77	841.3
1.148	481.3	12.20	576.3	31.99	697.9	51.91	788.2	71.54	861.7
3.813	506.4	16.67	608.7	36.71	722.2	56.84	807.7	76.59	881.3
6.924	534.3	21.48	639.9	41.83	745.9	62.07	826.9		
				373.15 K					
0.748*	443.1**	8.75	521.4	25.98	642.4	45.79	741.9	65.51	821.5
1.083	443.9	11.49	544.5	30.66	668.4	50.42	762.0	70.80	840.7
3.900	474.1	16.17	579.9	35.68	694.4	55.86	784.4	75.48	857.0
6.348	499.1	20.82	611.2	40.88	719.5	60.99	804.5		

[a] Values marked with an asterisk are vapor pressures p_s, from ref 6 for 283.15 to 323.15 K and 373.15 K. Those values marked with a double asterisk are extrapolated values at the given p_s.

Table III. Coefficients a_{ij} of Equation 1

i	a_{ij}, $j = 0$	$j = 1$	$j = 2$	$j = 3$
0	7.045549×10^{2}	5.924649	-3.663219×10^{2}	1.575744×10^{-4}
1	−3.589557	3.884995×10^{2}	-4.795983×10^{-4}	2.484617×10^{-6}
2	2.177083×10^{-5}	-6.082649×10^{-6}	4.142676×10^{-8}	

but the difference between u_{p_s} resulting from the inequality of p_s was only 0.1 m·s^{-1}. The uncertainty of u_{p_s} is estimated as ±0.35% after taking into account the errors caused by the absorption of the acoustic wave generated in the sample. Absorption phenomenon is frequently observed near the saturation boundary. Using the speed of sound u and density ρ, the

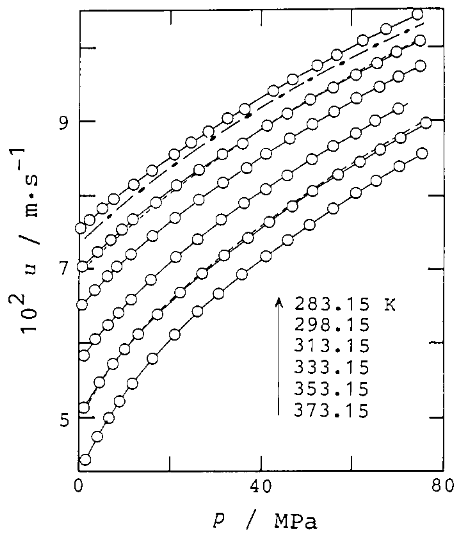

Figure 1. Pressure dependence of speed of sound u in various liquids: O, $CHClFCClF_2$ at various temperatures (present work); (–•–), CCl_3F at 298.15 K (*3*); (--), $CHCl_2CF_3$ at 298.15 and 353.15 K (*3*).

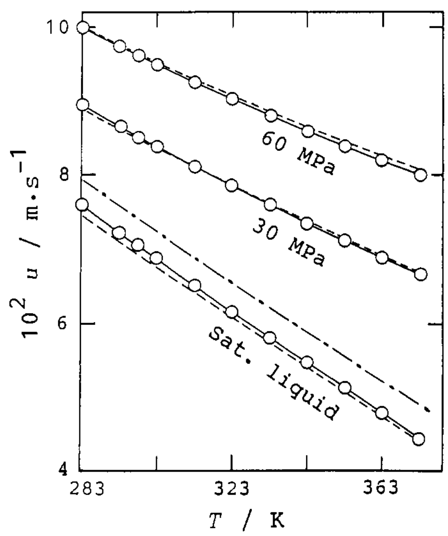

Figure 2. Temperature dependence of speed of sound u in various liquids: O, $CHClFCClF_2$ at various pressures (present work); (–•–), CCl_3F at 298.15 K (*3*); (--), $CHCl_2CF_3$ at 298.15 and 353.15 K (*3*).

isentropic compressibility for the saturated liquid was calculated from $\kappa_s = (\rho \cdot u^2)^{-1}$. The saturated liquid density used was that measured by Yokoyama et al. (*9*). The calculated values of κ_s as a function of temperature are shown graphically in Figure 3.

The differences in the speed of sound between the two ethane-based compounds is very small over the whole pressure range. However, the values of $(\partial u/\partial p)_T$ for $CHCl_2CF_3$ are greater than the corresponding values at the same temperature and pressure for $CHClFCClF_2$, as shown in Figures 1 and 2. In a previous paper (*3*), we speculated that the speed of sound is high for spherical molecules because spherical molecules can pack effectively in the liquid phase. This hypothesis is confirmed in this work because the speed of sound decreases in the order CCl_4 > CCl_3F > $CHCl_2CF_3$, that is, in the order of increasing nonsphericity of the molecules.

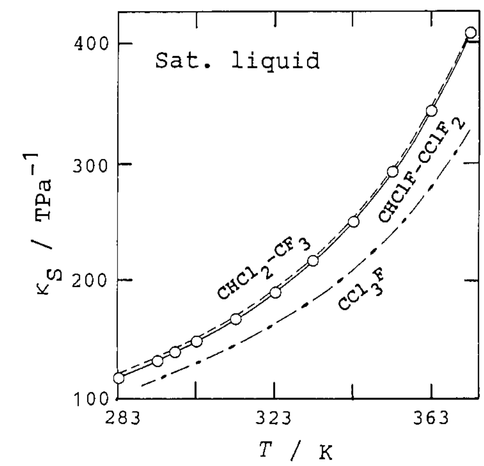

Figure 3. Temperature dependence of isentropic compressibility, κ_s, along the saturation curve: O, $CHClFCClF_2$ (present work); (–•–), CCl_3F (*3*); (--), $CHCl_2CF_3$ (*3*).

To examine the difference in the speed of sound between $CHCl_2CF_3$ and $CHClCClF_2$, the molar volumnes, V_0, at 0 K were estimated by Sugden's equation (*10*)

$$V_0 = V_T[1 - (T/T_c)]^{1/3} \quad (2)$$

where V_T is the molar volume at T K and T_c is the critical temperature. A small molar volume at 0 K indicates that there is efficient packing; hence, one would expect a higher speed of sound. From the densities listed in Table I, the following values for V_0 were obtained: 65.84 cm^3 mol^{-1} for CCl_3F, 76.66 cm^3 mol^{-1} for $CHClFCClF_2$, and 76.89 cm^3 mol^{-1} for $CHCl_2CF_3$. The small V_0 value for CCl_3F indicates that this compound should have a high value of u with a corresponding small pressure dependence, as shown in Figure 1. On the other hand, the value of V_0 for $CHClFCClF_2$ is slightly less than the value for $CHCl_2CF_3$, so little difference in the speed of sound for these two compounds is expected, while the pressure dependence of u and the isentropic compressibility are expected to be smaller for $CHClFCClF_2$ than for $CHCl_2CF_3$, as observed experimentally.

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