Ultrasonic Speeds in Compressed Liquid and Vapor Pressures for Pentafluoroethane

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Ultrasonic speeds in the liquid phase of pentafluoroethane, CHF_2CF_3, have been measured from 243.11 K to 333.15 K and pressures from near the saturation line to about 30 MPa. The measurement was carried out by means of a sing-around technique operated at a frequency of 2 MHz with an uncertainty no greater than ±0.2% in the high-density region. The vapor pressures have also been measured by monitoring the difference in the absorption quantity of the acoustic wave, excited in the sample fluid, between the liquid and gas phases with an uncertainty of ±10 kPa. From these results, the ultrasonic speeds for the saturated liquid were estimated with reasonable accuracy.

1. Introduction

As an alternative to the refrigerant chlorodifluoromethane, $CHClF_2$, some binary and/or ternary mixtures of hydrofluorocarbons have attracted attention. In an earlier paper, the author reported the ultrasonic speeds in the dense liquid for difluoromethane, CH_2F_2 (Takagi, 1993), and 1,1,1,2-tertrafluoroethane, CF_3CH_2F (Takagi, 1996). Pentafluoroethane, CHF_2CF_3, is an important component of possible mixtures, and the several properties for CHF_2CF_3 have been reported (Defibaugh and Morrison, 1992; Wilson *et al*., 1992; Ye *et al*., 1995).

In the present work, the ultrasonic speeds in the dense liquid and the vapor pressure for CHF_2CF_3 were measured over a temperature region from 243 K to 333 K covering from close to the boiling to the critical temperature and from close to the saturation line to up to about 30 MPa. The variation of these results with temperature and/or pressure is discussed.

2. Experimental Section

Chemicals. Two samples of CHF_2CF_3 were supplied by DuPont-Mitsui Fluoro-Chemicals Co., Ltd. (99.66+ mol %) and by Asahi Glass Co., Ltd. (99.98+ mol %).

Ultrasonic Speed. The ultrasonic speeds were measured using the sing-around technique employing a fixed path acoustic interferometer operated at a frequency of 2 MHz. The apparatus and the measurement method were described in detail in previous papers (Takagi, 1993, 1996). The transducer (PZT, 20 mm in diameter) for exciting the acoustic wave and reflector was held vertically by the spacer made of stainless steel in the high-pressure vessel. This vessel was immersed in a liquid thermostat controlled to within ±20 mK. The temperature was recorded by a quartz thermometer, which was calibrated within ±5 mK with a standard platinum thermometer, against ITS-90. The pressure generated by a hand oil pump was transmitted to the sample through a piston moving in the pressure vessel. The pressure was observed by two precision strain gauges of maximum pressure: (5 ± 0.003) MPa and (35 ± 0.005) MPa calibrated by a dead weight tester. The ultrasonic speed, $u\ [=2L/(t_2 - t_1)]$, was obtained by measuring the period, $(t_2 - t_1)$, between the first and second echoes of a short acoustic pulse traveling a known distance, L, between the transducer and reflector as the average value of 1000 periods. The value of $2L$, (47.602 ± 0.002) mm, was determined by measuring the period, t, in pure CCl_4 having the speed of sound of 921.11 $m{\cdot}s^{-1}$ at 298.15 K and 0.1 MPa. The effect of temperature changes on L was calculated from the expansion coefficient, $\alpha\ (=13.6 \times 10^{-6}\ K^{-1})$ of the stainless steel. The effect of pressure on the dimensions of the fixed path was neglected in the ranges of pressures up to 30 MPa.

Vapor Pressure. The vapor pressure was measured by monitoring the difference in the absorption quantity of the acoustic wave between the liquid and gas phases, excited in the sample for the speed measurement. When the liquid level at the vapor−liquid equilibrium was located close to the bottom position of the transducer, that is, a large absorption was monitored, the pressure was observed by a precision strain gauge. The sensitivity of the Teflon capsule of 0.2 mm thickness used as the sample−oil separator to pressure changes was within ±0.003 MPa. The strain gauge transducer was held at constant temperature by a water jacket.

The pressure gauge had a measuring range of 5 MPa and a resolution of 800.00 mV/MPa that was stable to ±0.1 mV, corresponding to a stability in the pressure measurement of ±0.12 kPa.

3. Results and Discussions

The results of ultrasonic speeds, u, in the liquid phase of pentafluoroethane, CHF_2CF_3, measured with a sample purity of 99.67+% are listed in Table 1 and plotted in Figure 1.

To determine the effect of sample purity, the measurements at a sample purity of 99.96 + mol % were made at 298.12 K. For sample purities of 99.67 and 99.96+ mol %, the values of u are (368.8 and 369.9) $m{\cdot}s^{-1}$ at 3.618 MPa and (535.2 and 536.1) $m{\cdot}s^{-1}$ at 20 MPa, respectively. The result of u in the high-grade sample is slightly higher than that for the former sample at each pressure. But the differences between both samples are only 1 $m{\cdot}s^{-1}$ in u.

It seems reasonable that these are due to the experimental error rather than are affected by the impurities in the samples.

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Table 1. Ultrasonic Speeds, *u*, in the Liquid Phase for Pentafluoroethane 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}
T = 241.15 K							
0.229	599.0	2.946	621.9	9.417	666.7	22.143	739.4
0.308	601.4	3.469	625.9	11.496	679.5	24.696	752.5
0.522	603.2	4.929	636.3	13.567	691.9	27.039	765.3
1.081	607.7	5.935	643.4	15.851	705.1	29.815	777.2
1.446	610.4	7.183	651.9	17.945	717.0		
1.977	614.6	8.947	663.4	20.178	729.2		
T = 253.14 K							
0.338	545.3	2.821	568.0	10.991	629.4	22.265	698.1
0.622	547.9	3.467	573.4	12.275	638.0	24.860	712.2
0.871	550.5	4.341	580.4	14.539	652.6	27.140	724.2
1.231	553.8	5.590	590.1	15.793	660.3	30.014	738.6
1.624	557.4	7.158	601.9	17.331	669.8		
2.259	563.1	9.231	617.0	19.722	683.6		
T = 263.24 K							
0.662	500.7	3.078	524.7	9.399	577.9	22.538	665.1
0.910	503.2	3.522	528.7	11.809	595.7	24.479	676.1
1.213	506.4	4.103	534.1	14.091	611.6	27.043	689.9
1.491	509.2	4.905	541.0	16.203	626.1	29.412	702.9
2.038	514.7	5.762	548.4	18.625	641.4	30.824	710.2
2.606	520.2	6.851	557.5	20.817	654.9		
T = 273.13 K							
0.679	451.6	5.373	502.7	15.111	583.1	28.565	667.3
1.114	457.1	6.933	517.4	16.806	595.1	31.462	683.1
1.353	459.9	9.275	538.0	18.675	607.7		
1.559	462.5	11.184	553.5	20.150	617.2		
2.278	470.7	12.830	566.4	22.317	630.9		
3.892	487.9	14.704	580.1	24.645	644.9		
T = 283.13 K							
1.208	407.6	5.536	460.8	14.757	544.9	26.984	627.3
1.539	412.4	7.298	479.2	17.069	562.4	29.926	644.5
2.004	419.4	8.711	493.3	20.216	584.5	32.086	656.4
2.950	430.5	10.052	505.8	22.261	598.0		
4.013	443.8	11.834	521.3	24.438	611.8		
T = 298.21 K							
1.569	332.8	4.497	381.0	14.538	490.9	26.975	582.6
2.163	344.0	5.735	398.2	16.994	511.4	29.784	600.1
2.631	352.4	7.728	422.9	19.767	533.0		
3.417	365.1	9.893	446.7	22.121	550.2		
4.170	376.6	11.914	466.9	24.754	568.0		
T = 298.12 K[a]							
3.423	366.1	10.267	451.5	19.949	535.5	29.798	601.2
4.745	385.9	12.048	468.4	22.049	550.7	32.187	615.4
6.728	411.8	14.620	492.7	24.876	570.1		
8.924	437.5	17.134	513.7	27.156	584.4		
T = 313.13 K							
2.954	278.0	6.509	345.3	14.106	437.7	24.539	524.7
3.386	287.8	7.686	362.7	15.773	453.7	26.085	535.6
3.864	300.0	8.763	377.8	18.149	474.8	28.705	553.3
4.358	310.5	9.972	392.9	19.910	489.4	30.300	563.6
5.632	332.3	11.948	415.2	22.012	506.0		
T = 333.11 K							
7.315	277.7	11.020	337.3	17.400	411.3	24.755	475.1
8.039	291.5	12.930	362.6	19.405	430.4	27.193	493.4
9.676	318.1	14.911	385.4	22.391	456.2	29.793	512.0

[a] Remeasured at the sample purity of 99.96+ mole % supplied by Asahi Glass Co., Ltd.

The u data are represented as a function of temperature, T, and pressure, p, by the following polynomial equation:

$$u/\mathrm{m{\cdot}s^{-1}} = \sum_{j=0}^{4}\sum_{j=0}^{4} a_{ij}(T/\mathrm{K} - 273.15)^{i}\,(p/\mathrm{MPa} - 5)^{j} \quad (1)$$

The values of the coefficients a_{ij} were calculated by least-squares analysis of the 155 data points including the 14 points at 298.12 K above 350 m·s^{-1} weighted equally. The coefficients are given in Table 2.

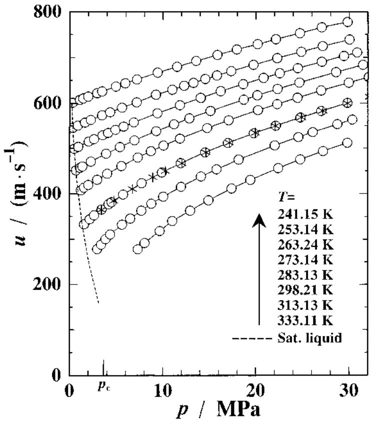

Figure 1. Pressure, p, dependence of ultrasonic speeds, u, in the liquid phase of pentafluoroethane: (- - -) calculated from eq 3; (∗) remeasurement values at 298.12 K.

This equation reproduces the experimental values with a mean deviation δ_{mean} of 0.06. The largest deviation from eq 1, −0.4%, occurs in the vicinity of the saturation line close to the critical temperature, where the values are very pressure dependent. For the present refrigerant, an absorption of the acoustic wave was smaller than that for CF_3CH_2F (Takagi, 1996). But that was gradually increased around the experimental condition result below 350 m·s^{-1}, and measurement near the critical region became impossible. Therefore the u values below 350 m·s^{-1} generally have very large experimental errors and were unused in the determination of eq 1. In the high-density region the values of u were reproduced within an accuracy of ±0.3 m·s^{-1} in repeated runs. The accuracy in the present u values in the range 243 K to 333 K was estimated to be within ±0.2% except for values lower than 350 m·s^{-1}.

The vapor pressure p_s for CHF_2CF_3 was measured using the same apparatus by monitoring the liquid level. The pressure was measured by a precision strain gauge through a strain of a Teflon capsule of 0.2 mm thickness used as the sample−oil separator. The mean results, $p_{s(T)}$ of four or five in repeated runs with a sample purity of 99.67+ mol % are listed in Table 3. In this table, the vapor pressure values measured at 298.12 K for the sample with purity better than 99.96 mol % are also included. When these values are compared at 298.12 and 298.21 K, they depend on the temperature change, and that difference cannot discriminate one sample purity from the other.

The vapor pressure, p_s, results in the ranges from 243 K to 333 K were correlated with the following Wagner-type equation:

$$\ln(p_s/p_c) = (1/T_r)[-7.12839(1 - T_r) + 0.293508(1 - T_r)^{1.5} + 0.59185(1 - T_r)^{3}] \quad (2)$$

where p_c is the critical pressure the $T_r = T/T_c$ is the reduced temperature. The values of T_c and p_c for the present substance are 339.17 K and 3.618 MPa, respectively. The values $P_{s(C)}$ calculated from eq 2 are well reproduced with the experimental results, $P_{s(T)}$ within ±10 kPa. For this compound, many data sets on the vapor pressure are available. The most reliable values are evaluated by Sato *et al.* (1994). Boyes and Weber (1995) measured the accurate vapor pressure to within ±0.1 kPa in the range of 273 K to 363 K. As shown in Table 3, the present experimental results, $p_{s(T)}$ are in good agreement with these reference data of $p_{s(S)}$ and $p_{s(B)}$ to within ±10 kPa.

The ultrasonic speeds, u_s, for the saturated liquid were obtained by extrapolation to the vapor pressure. The application of eq 1 to obtain u_s close to the critical

Table 2. Coefficients, a_{ij}, of Eq 1 and Mean Deviation δ_{mean} in the Liquid Phase for Pentafluoroethane[a]

	i			
j	0	1	2	3
0	4.987007×10^{2}	-4.385646	-1.496521×10^{-3}	1.689585×10^{-5}
1	9.917364	1.221425×10^{-1}	1.090980×10^{-3}	
2	-2.016320×10^{-1}	-5.395294×10^{-3}	-7.375148×10^{-5}	
3	5.042481×10^{-3}	1.378164×10^{-4}	2.525364×10^{-6}	
4	-6.219740×10^{-5}	-1.323322×10^{-6}	-3.570740×10^{-8}	

[a] $\delta_{\text{mean}} = 0.061$, $\delta_{\text{mean}} = |100(u_{\text{exp}} - u_{\text{calc}})/u_{\text{calc}}|/n$, where $n(=155)$ is the number of data points.

Table 3. Comparison of Vapor Pressure, p_s, for Pentafluoroethane with Literature Values[a]

	MPa			
T/K	$p_{s(T)}$	$p_{s(C)}$	$p_{s(S)}$	$p_{s(B)}$
241.15	0.221 ± 0.005	0.217		
253.14	0.338 ± 0.002	0.341	0.337	
263.24	0.483 ± 0.004	0.486	0.484	
273.13	0.675 ± 0.001	0.670	0.670	0.670
283.13	0.913 ± 0.003	0.906	0.908	0.908
298.21	1.380 ± 0.002	1.380	1.379	1.380
298.12[b]	1.376 ± 0.004	1.376	1.376	1.376
313.13	2.010 ± 0.004	2.014	2.006	2.008
333.11	3.171 ± 0.006	3.180	3.169	3.168

[a] $p_{s(T)}$, this work, average values of many data points. $p_{s(C)}$, calculated from eq 2. $p_{s(S)}$, Sato *et al.* (1994). $p_{s(B)}$, Boyes and Weber (1995). [b] Values remeasured using the sample purity of 99.96+ mol %.

Table 4. Comparison of Ultrasonic Speeds at the Saturation Line, u_s, for Pentafluoroethane with Literature Values

	$\text{m} \cdot \text{s}^{-1}$			
T/K	$u_{s(T)}$	$u_{s(C1)}$	$u_{s(C2)}$	$u_{s(K)}$
241.15	600.2	600.1	600.1	
253.14	545.3	545.5	545.7	
263.24	498.7	498.6	498.6	
273.13	452.0	451.9	451.6	
283.13	404.3	404.1	403.9	
298.21	330.7	330.7	330.7	327.5
298.12[b]	339.6	331.2	333.5	
313.13	259.9	257.1*	267.3	251.5
333.11	209.2	156.9*	192.5	127.9

[a] $u_{s(T)}$, obtained from the data for the low-pressure range by extrapolation to the saturation line. $u_{s(C1)}$, calculated from eq 3; * refer to extrapolated values from eq 3. $u_{s(C2)}$, calculated from eq 1. $u_{c(K)}$, calculated from data reported by Kraft and Leipertz (1994). [b] Values remeasured using the sample purity of 99.96+ mol %.

temperature was far from satisfactory. Therefore, the saturated liquid values were obtained by an appropriate quadratic equation using about 10 data points in the lower pressure range and were listed in Table 4. It appears that these values decrease, indicating a concave curve, with increasing temperature and come close to the minimum value of around 100 $\text{m} \cdot \text{s}^{-1}$ at the critical point. The u_s estimated at 313 K and 333 K deviates largely from a smooth curve, because it is lacking the data points near the saturation line. The results of u_s in the range from 243 K to 298 K was fitted by following equation:

$$u_s/\text{m} \cdot \text{s}^{-1} = 2252.24 - 202.046 T_r^{-1} - 1923.98 T_r \quad (3)$$

where T_r $(=T/T_c)$ is reduced temperature. Kraft and Leipertz (1994) measured the ultrasonic speeds in the saturated liquid and gas for perfluoroethane at high temperatures including the critical point by a dynamic light scattering technique with an uncertainty of ±0.5%. At 298.21 K the present value is in agreement with the value of Kraft and Leipertz within 3 $\text{m} \cdot \text{s}^{-1}$ (see Table 4 and Figure 2). The values u_{pc} at the critical pressure (3.618 MPa), estimated by the above manner, are given in Figure 2. These are also suggested to come close to the minimum value at the critical point. The temperature dependence of ultrasonic speed, $(\partial u/\partial T)_p$, at pressures above p_c calculated from eq 1 differs largely from those at p_s and p_c lines, especially near the critical temperature.

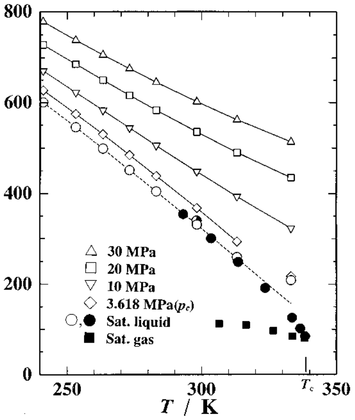

Figure 2. Temperature, *T*, dependence of ultrasonic speeds, *u*, in the liquid phase of pentafluoroethane: (△, □, ▽) calculated from eq 1; (- - -) calculated from eq 3; (◇, ○) estimated from data at the lower pressures region; (◑) estimated from remeasurement values; (●,■) Kraft and Leipertz (1994).

Piao and Noguchi (1995) have developed a modified Benedict−Webb−Rubin equation of state for pentafluoroethane using available *PVT* and vapor−liquid equilibria, data which are applicable to the wide range from 170 K to 475 K and pressures up to 68 MPa. That equation used the ultrasonic speed values presented here to confirm the reliability of the equation of state, and they reported ±1.3% in the ultrasonic speed between these experimental values and those derived from the equation of state.

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