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Ultrasonic Speeds in Liquid 1,1,1-Trifluoroethane under High Pressures

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Ultrasonic speeds in the liquid phase of 1,1,1-trifluoromethane, CF_3CH_3, have been measured by a sing-around technique operated at a frequency of 2 MHz. The experimental results were obtained along eight isotherms from 243 to 333 K at pressures from near the saturation line to about 30 MPa. The probable uncertainty in the results was within ±0.2% in the high-density region. These results are used for comparison with those for other hydrofluorocarbons, and it is found that the absolute values for those substituted decrease in the order $CF_3CH_3 > CF_3CH_2F > CF_3CHF_2$ over the whole range of conditions, corresponding to the increasing number of fluorine atoms.

1. Introduction

The author has reported previously ultrasonic speeds in the liquid phase of three hydrofluorocarbons, difluoromethane, CH_2F_2 (HFC32, Takagi, 1993), 1,1,1,2-tetrafluoroethane, CF_3CH_2F (HFC134a, Takagi, 1996a), and pentafluoroethane, CF_3CHF_2 (HFC125, Takagi, 1996b), which are important refrigerants as replacements for chlorodifluoromethane, $CHClF_2$ (HCFC22), measured over wide temperature and pressure ranges. These results give a powerful clue to the measurement of thermodynamic characteristics for each substance.

1,1,1-Trifluoroethane, CF_3CH_3 (HFC143a), is considered as a safe environmental substance, but its use on its own is inconvenient because of its flammability due to the presence of hydrogen atoms. In many applications, CF_3CH_3 is valuable as a component of binary or ternary mixtures. In this work, the ultrasonic speed in the liquid phase of 1,1,1-trifluoroethane was measured at temperatures from 243 to 333 K, covering the range from near the normal boiling point to near the critical temperature, and at pressures from near the saturation line to about 30 MPa with an uncertainty of ±0.2 % in the high-density region. The temperature and pressure behavior is compared with that for other hydrofluorocarbons reported previously.

2. Experimental Section

Chemicals: A pure sample of 1,1,1-trifluoroethane, CF_3CH_3, was supplied by Daikin Industrials Ltd. The purity was better than 99.96+ mol %, as measured by GLC.

Ultrasonic Speed. The ultrasonic speeds were measured using the sing-around technique employing a fixed path interferometer operated at a frequency of 2 MHz, similar to that outlined previously (Takagi, 1993, 1996a). The pressure vessel containing an acoustic interferometer was immersed in a liquid thermostat controlled to within ±20 mK. The temperature was given by a quartz thermometer, which was calibrated within ±5 mK with a standard platinum thermometer againat ITS-90. The pressure in the sample was observed by two precision strain gauges of maximum pressure: (5 ± 0.003) MPa (Nagano Keiki Co., KH15) calibrated by a quartz crystal pressure transducer and (35 ± 0.005) MPa (Tsukasa Sokken Co., PH-22-G) calibrated by a dead weight tester.

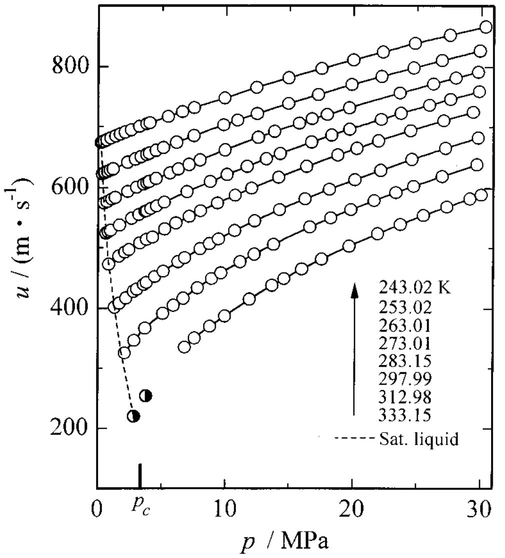

Figure 1. Pressure, p, dependence of ultrasonic speeds, u, in the liquid phase of CF_3CH_3. ◑, estimated graphically from the speeds for saturated liquid and for the high-pressure region at 333.15 K.

The ultrasonic speed, u [$=2L/(t_2 - t_1)$] was obtained by measuring the period between the first, t_1, and second, t_2, echoes of a short acoustic pulse traveling a known distance, L [(23.801 ± 0.002) mm at 298.15 K and 0.1 MPa], between the transducer and reflector. The values of $(t_2 - t_1)$ were recorded by a universal counter with a resolution of 0.1 ns as the average value of 1000 periods.

3. Results and Discussion

The experimental ultrasonic speeds, u, in the liquid phase of 1,1,1-trifluoroethane, CF_3CH_3 at various temperatures, T, and pressures, p, are presented in Table 1 and Figure 1. For the present refrigerant, no experimental study of the ultrasonic speed in the liquid phase has previously been made. The reliability of the instrument used in this work was previously tested by measuring the u values. That is, the experimental values were in good agreement in the compressed liquid CF_3CH_2F (Takagi, 1996a), for example, within 0.7 m·s^{-1} at 298.15 K and 10 MPa and in the saturated liquid CF_3CHF_2 (Takagi, 1996b) within 3 m·s^{-1} at 298.15 K with reference values reported elsewhere. The difference of period $(t_1 - t_2)$ between the

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Table 1. Ultrasonic Speeds, *u*, in the Liquid Phase for CF_3CH_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})
$T = 243.02$ K							
0.209^a	674.0^b	1.697	687.4	6.56	724.7	22.31	824.6
0.248	674.2	2.084	690.6	7.49	731.5	24.81	838.9
0.324	675.1	2.568	694.2	9.90	747.7	27.54	852.8
0.440	676.2	3.208	700.0	12.39	765.7	30.32	866.7
0.645	678.0	3.769^c	704.2^b	14.92	781.6		
0.967	680.9	4.016	705.9	17.50	797.2		
1.364	684.5	5.45	716.7	20.00	811.5		
$T = 253.02$ K							
0.310^a	623.0^b	2.883	647.0	7.47	684.8	22.21	784.2
0.455	624.3	3.327	650.7	9.80	702.6	24.71	798.6
0.527	625.5	3.769^c	654.6^b	10.90	710.7	26.91	810.9
0.715	626.8	3.983	656.4	12.45	721.7	29.89	826.9
0.937	629.0	4.504	660.9	14.91	738.5		
1.145	630.9	5.08	665.5	17.24	753.7		
2.281	641.6	6.11	674.1	19.87	770.1		
$T = 263.01$ K							
0.438^a	573.9^b	3.527	605.8	7.96	645.5	19.68	731.7
0.450	574.2	3.769^c	608.1^b	9.912	661.8	23.650	756.7
0.675	576.5	3.964	610.1	12.53	682.4	26.255	772.2
1.050	580.6	4.505	615.2	13.81	691.9	28.004	782.2
1.319	583.5	5.59	624.2	15.76	705.7	29.760	792.1
2.279	593.4	6.24	630.6	16.84	713.2		
2.989	600.6	7.09	638.1	17.94	720.3		
$T = 273.01$ K							
0.606^a	523.9^b	3.659	560.3	10.08	622.0	22.18	712.5
0.617	524.8	3.769^c	561.3^b	11.66	635.3	23.73	722.8
0.774	526.6	4.097	564.9	13.16	647.6	25.95	736.6
0.962	529.1	4.540	569.3	14.25	656.1	27.58	746.5
1.657	537.4	5.15	575.6	16.72	674.6	29.84	759.8
2.610	548.7	6.92	593.2	18.30	686.0		
3.166	554.8	8.76	610.2	19.70	696.0		
$T = 283.15$ K							
0.823^a	472.7^b	4.245	517.7	12.01	599.2	27.06	710.7
1.181	474.9	5.19	530.9	14.13	617.5	29.37	725.2
1.613	486.1	6.07	540.9	16.33	635.2		
2.089	492.6	7.11	551.9	18.78	653.9		
2.403	496.9	8.00	561.3	20.27	664.8		
3.261	507.8	9.33	574.4	21.97	677.0		
3.769^c	513.7^b	10.72	587.5	24.47	693.9		
$T = 297.99$ K							
1.299^a	401.9^b	4.427	452.0	10.69	528.7	24.58	647.1
1.661	408.4	5.09	461.0	12.25	544.6	27.20	665.4
2.174	416.8	6.25	476.7	14.21	563.4	29.76	682.3
2.762	427.6	6.77	483.3	16.21	581.4		
3.031	431.3	7.97	498.3	18.12	597.7		
3.566	438.9	8.71	506.8	20.12	613.8		
3.769^c	442.4^b	9.42	514.8	22.14	629.2		
$T = 312.98$ K							
1.807^a	325.8^b	5.904	405.1	12.23	489.5	23.33	592.7
2.074	328.9	6.66	416.5	13.75	505.9	24.71	603.3
2.820	347.1	7.78	433.2	16.59	534.5	26.93	619.8
3.686	367.5	8.89	448.6	18.24	549.9	29.66	639.1
3.769^c	365.9^b	9.62	458.1	19.81	563.7		
5.072	392.0	11.13	476.7	21.63	578.9		
$T = 333.15$ K							
2.837^a	220.3^d	9.93	387.5	17.53	481.4	27.31	568.7
3.769^c	284.1^d	11.88	415.0	19.69	503.0	29.12	582.6
6.791	335.6	13.64	437.5	21.91	523.7	30.01	589.2
7.56	351.0	14.58	448.7	23.68	539.2		
8.76	370.7	15.98	464.7	25.48	554.3		

[a] Vapor pressure. [b] Estimated from data at low pressure. [c] Pressure corresponding to the critical pressure. [d] Estimated graphically.

first and second echoes observed for the present compound was from 54.9206 to 144.6927 μs, with a stability of ±0.0018 μs, except for the low-density region at high temperature. The probable uncertainty in the present results was no greater than ±0.2 % for the high-density region, taking into account the errors in the temperature and pressure measurements and that caused by the path length, *L*.

The present ultrasonic speeds, *u*, were fit on smooth curves for each isotherm, as shown in Figure 1, and can be represented as a function of temperature, *T*, and pressure, *p*, by the following polynomial equation

$$u/(\mathrm{m \cdot s^{-1}}) = \sum_{i=0}^{4} \sum_{j=0}^{4} a_{ij} T_r^{\,i} p_r^{\,j} \qquad (1)$$

Table 2. Coefficients a_{ij} of Eq 1 and Mean Deviation δ_{mean}[a] in the Liquid Phase of CF_3CH_3

	i			
j	0	1	2	3
0	$2.590\,161 \times 10^3$	$-4.546\,779 \times 10^3$	$3.842\,563 \times 10^3$	$-1.788\,105 \times 10^3$
1	$137.034\,5 \times 10^2$	$-4.450\,715 \times 10^2$	$4.215\,676 \times 10^2$	
2	$1.565\,195 \times 10^1$	$-2.169\,719 \times 10^1$	$-4.327\,624$	
3	$-5.398\,682$	$1.294\,673 \times 10^1$	$-7.181\,999$	
4	$2.968\,087 \times 10^{-1}$	$-7.773\,961 \times 10^{-1}$	$4.836\,365 \times 10^{-1}$	

[a] $\delta_{mean} = 0.102$, $\delta_{mean} = |100\Sigma[(u_{exp} - u_{calc})/u_{calc}]|n$, where n (=169) is number of data points.

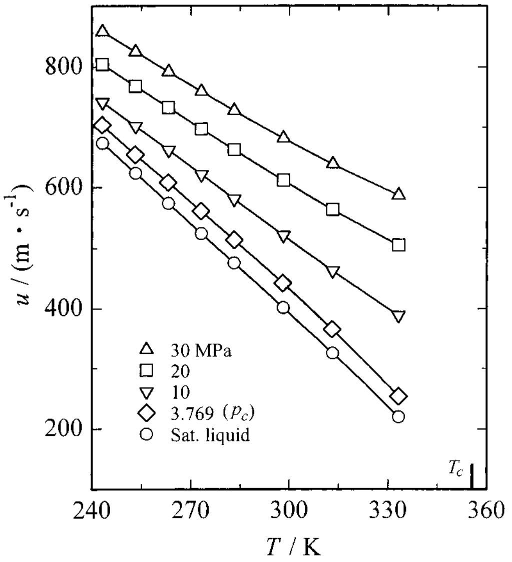

Figure 2. Temperature, T, dependence of ultrasonic speeds, u, in the liquid phase of CF_3CH_3.

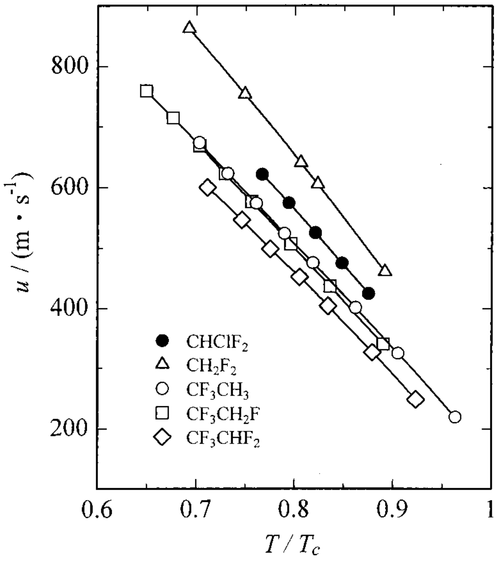

Figure 3. Ultrasonic speeds, u, in the saturated liquid of several compounds against reduced temperature, T/T_c.

where T_r and p_r are the reduced temperature T/T_c, and pressure, p/p_c, respectively. The values of the coefficients, a_{ij}, were calculated by least-squares analysis of 169 data points above 400 $m{\cdot}s^{-1}$ weighted equally and are listed in Table 2. This equation reproduces well the experimental values with a mean deviation, δ_{mean}, of 0.102. The larger deviation from the above equation, maximum −0.3 %, occurs mainly near the saturation line at high temperature, where the u values are strongly dependent on the temperature and pressure changes. The critical temperature and pressure for this compound are 345.97 K and 3.769 MPa, respectively, (JAR Tables, 1994). Close to the critical temperature, the uncertainty in the experimental u was sharply increased with greater absorption of the acoustic wave excited in the sample, especially near the saturation line. The present data observed below 400 $m{\cdot}s^{-1}$ include a large uncertainty and so were neglected in the application of eq 1.

From the experimental results, the ultrasonic speed, u_s, for the saturated liquid was estimated. Equation 1 did not apply satisfactorily to the results around the saturation line, especially those in the high-temperature region, as described above. In this work, those values were estimated by extrapolation to the vapor pressure, p_s, from about 10 data points in the low-pressure range, which were measured at narrow pressure intervals. The p_s value required in this calculation was derived from the equation correlated by the JAR Tables (1994). The values u_{pc} at 3.769 MPa corresponding to the critical pressure, p_c, were also determined in a similar way, and those for u_s, are also presented in Table 1. The u_s and u_{pc} values at 333 K, where the data around the saturation line was poor, were estimated graphically from Figures 1 and 2. With increasing temperature, the curves of both u_s and u_{pc} decrease in parallel at first, and they converge finally to a minimum of around 100 $m{\cdot}s^{-1}$ at the critical point. The estimated u_s value in the range from 241 to 298 K can be rearranged as a function of temperature by the following equation:

$$u_{s(c)}/(m{\cdot}s^{-1}) = 523.3 - 4.945t + 2.718 \times 10^{-3}\, t^2 \quad (2)$$

where $t = T/K - 273.15$. The $u_{s(c)}$ were reproduced within ±1.5 $m{\cdot}s^{-1}$ to the estimated u_s values, as plotted by the dotted line in Figures 1 and 2. The isobaric data at 10, 20, and 30 MPa calculated from eq 1 are indicated by the concave curves.

The ultrasonic speeds, u, for the principal safe hydrofluorocarbons; CH2F2, CF_3CH_2F, and CF_3CHF_2, have been reported previously. For those substances, including CF_3CH_3 presented here, the temperature and pressure effects on the speed of sound, u_s, in the saturated liquid is shown in Figure 3 against reduced temperature T/T_c. The speed at $0.8T_c$ was calculated for each substance, and their pressure dependence is illustrated graphically in Figure 4. As can be seen in these figures, the u for methane fluid shows higher values compared with values in methane-based substances. On the other hand, for ethane-based fluids the speeds u indicate an interesting dependence on the pressure. The absolute decrease in u in the order CF_3CH_3 > CF_3CH_2F > CF_3CHF_2 corresponds to the increasing number of fluorine atoms in the molecules. However, the pressure dependence of speed u, $(\partial u/\partial p)_{0.8T_c}$, in CF_3CH_3 presented here is found to be significantly different from the other two substances over the whole range of conditions.

It is contemplated that these hydrofluorocarbons, which possess a large dipole moment as listed in Table 3, have a strong intramolecular interaction. But in many cases of fluids having interaction, the prssure effects on the thermophysical properties are generally weak. On the other

Table 3. Ultrasonic Speed, u_s, Its Pressure Effects, $(\partial u/\partial p)_{T(ps)}$, and Isentropic Compressibility, $\kappa_{s(s)}$, in the Saturated Liquid for Several Substances at Temperature of $0.8T_c$

substance	T_c, K	$0.8T_c$, K	p_s, MPa	u_s, m·s^{-1}	$(\partial u/\partial p)_{T(ps)}$, m·s^{-1}·MPa^{-1}	ρ_s, kg·m^{-3}	$\kappa_{s(s)}$, GPa^{-1}	μ,[b] D
$CHClF_2$[c]	369.39	295.44	0.971	563	10.9	1206	2.61	1.42[d]
CH_2F_2[e]	351.26	281.01	1.039	653	10.6	1073	2.18	1.98[d]
CF_3CH_3[f]	339.17	276.78	0.693	505	13.3	1007	3.98	2.340
CF_3CH_2F[g]	374.27	299.41	0.691	500	12.0	1200	3.32	2.058
CF_3CHF_2[h]	345.97	271.34	0.633	460	11.6	1328	3.56	1.563

[a] Critical temperature, T_c, vapor pressure, p_s, and saturated density, ρ_s (JAR Tables, 1995). [b] Dipole moment, μ, Meyer and Morrison (1991). [c] Takagi (1993). [d] Thermophysical Properties Handbook (1990). [e] Takagi (1993). [f] Takagi (1996a). [g] This work. [h] Takagi (1996b).

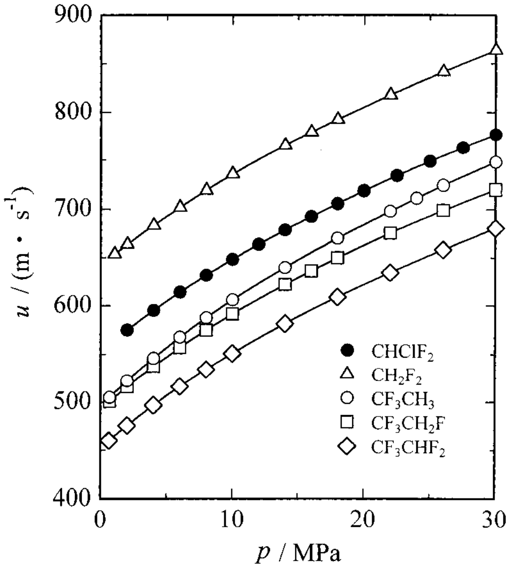

Figure 4. Pressure, p, dependence of ultrasonic speeds, u, in the liquid phase of several compounds at $0.8T_c$.

hand, the speed of the acoustic waves excited in the sample depends on compression properties, and that is much more subject to the intermolecular free volume in molecules (Pouling, 1960). The van der Waals radius of hydrogen and fluorine atoms is 1.20 and 1.35 nm, respectively. The increased values of $(\partial u/\partial p)_{0.8T_c}$ for CF_3CH_3 can be attributed to the antisymmetric structure in the these ethane-based compounds. This phenomenon is also supported qualitatively by the large value of isentropic compressibility, κ_s, as obtained experimentally.

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