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Ultrasonic speeds in dense liquid of $1,1,1,2,2$ -pentafluoro-3,3-dichloropropane and 1,1,2,2,3-pentafluoro-1,3-dichloropropane

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Abstract

The ultrasonic speeds in the liquid phase of 1,1,1,2,2-penta $fluoro-3,3$ -dichloropropane, $CF_3CF_2CHCl_2$ and 1,1,2,2,3pentafluoro-1,3-dichloropropane, CClF₂CF₂CHClF, which have been developed as new cleaning agents, were measured by a sing-around technique operated at a frequency of 2 MHz. The measurements were carried out at $283-343$ K and pressures up to 30 MPa with an uncertainty within $\pm 0.2\%$. The results for each isotherm show the linear relation with densities and are correlated by the Tait equation with a reasonable accuracy in the whole range of conditions. It is found that these substances, showing lower ultrasonic speed similar to that in 1,1,2-trichloro-1,1,3-trifluoroethane, CCl_2FCClF_2 have excellent characteristics of cleaning agents. \odot 1998 Elsevier Science B.V.

Keywords: Ultrasonic speed; High pressure; $CF_3CF_2CHCl_2$; $CCIF_2CF_2CHClF$; Cleaning agents

1. Introduction

Several new cleaning agents have been developed as replacement compounds for 1,1,2-trichloro-1,2,2 trifluoroethane (CCl₂FCClF₂, CFC-113), which has a strong ozone depletion potential (ODP= $0.8 \sim 0.9$). In the precision industry (micro-electronics and precision machinery) they are used as solvents for ultrasonic cleaning, and therefore the ultrasonic speed in the fluid is an important property in order to analyze the mechanism of the cleaning process. In a previous paper, Takagi and Noguchi [1] measured the ultrasonic speed at several temperatures and pressures in the liquid phase of $2,2,3,3,3$ -pentafluoro-1-propanol $(CF₃CF₂CH₂OH, 5FP)$, which is one of the powerful new cleaning agents.

In the present work, the ultrasonic speed, u in the liquid phase of $1,1,1,2,2$ -pentafluoro-3,3-dichloropropane $(CF_3CF_2CHCl_2$, HCFC 225 ca) and 1,1,2,2,3pentafluoro-1,3-dichloropropane (CClF₂CF₂CHClF, HCFC225 cb) was measured at temperatures from 283 to 333 K and pressures up to 30 MPa. The results are correlated by the Tait equation with a reasonable accuracy in the whole range of measurements. The temperature and pressure effects of these u values are discussed with those of CCl_2FCClF_2 and $CF₃CF₂CH₂OH.$

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2. Experimental

2.1. Chemicals

The samples were purified products from Asahi Glass, and had purities greater than 99.99 mol%. These substances were used without further purification expect that they were carefully dried with molecular sieve 5A supplied by Wako Pure Chemicals. The physical properties of these substances are listed in Table 1 together with those for CCl_2FCClF_2 and $CF₃CF₂CH₂OH.$

2.2. Ultrasonic speed

The ultrasonic speed, u was measured using the sing-around method operated at a frequency of 2 MHz, similar to that described in the previous papers

Table 1

Physical properties for each substance

of Takagi [1,9]. The acoustic interferometer used in this work is illustrated in Fig. 1. The pressure vessel containing interferometer was immersed in a liquid thermostat controlled to within ± 20 mK. The temperature was measured by a quartz thermometer with a resolution of ± 1 mK. This thermometer was calibrated within ± 5 mK using a standard platinum thermometer (ITS-90) by the National Research Laboratory of Metrology (Japan). The pressure generated by a hand-oil-pump was transmitted to the sample through the strain of a Teflon capsule, and was measured by a precision strain gauge (maximum pressure of 35 MPa). The gauge was held in a constant temperature by a bobbin heater controlled within 308 ± 2 K. That was calibrated using a quartz pressure gauge within ± 8 kPa at lower pressure region, and using a dead weight gauge at higher pressure range within ± 15 kPa.

ODP: Ozone depletion potential; p_s : Vapor pressure; ρ : Density; u: Ultrasonic speed; κ_T : Isothermal compressibility; κ_s : Isentropic compressibility; γ : Ratio of specific heat capacities. C_p : isobalic specific heat capacity; η : Viscosity; λ : Thermal conductivity; ζ : Acoustic absorption: f: Frequency.

^a values for CF₃CF₂CH₂OH are at 0.1 MPa reported in [1], and for CCl₂FCClF₂ estimated from data in [2]. b See [3].

 c See [4].

 d See [5]

^e See [6].

^f See [7].

 g See [8].

Fig. 1. Acoustic interferometer. $L=23.801\pm0.002$ mm at 298.15 K and 0.1 MPa.

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 $(23.801 \pm 0.002$ mm at 298.15 K and 0.1 MPa) between the transducer and reflector held in parallel position by a stainless steel support. The values of (t_2-t_1) were recorded by a universal counter with a resolution of 0.1 ns as an average value of 1000 periods. Where the delay time in the singaround circuit was fixed to 255.636 ± 0.0009 µs, and the observed values of (t_2-t_1) were between 56 and 82 ± 0.002 µs in the both samples presented here. The influence of temperature on L was evaluated from the thermal expansion coefficient of stainless steel, but that of the pressure was neglected. The probable uncertainty in the measurements taking into account the measurement errors of temperature $(\pm 20 \text{ mK})$ and pressure (\pm 15 kPa) was within \pm 0.2% at all conditions.

3. Results and discussion

The experimental values of ultrasonic speed, u in the liquid phase of $CF_3CF_2CHCl_2$ and $CCIF_2$ - $CF₂CHCIF$ are presented in Table 2. The values of u along each isotherm increase monotonously with increasing pressure as can be seen in Figs. 2 and 3. For the present compounds, no experimental study of the ultrasonic speed in the liquid phase has been previously reported. The authors therefore, measured the u values in pure tetrachloromethane and benzene at various conditions of temperature and pressure, and confirmed the reliability of the instrument by comparison with the accurate values measured by Bobik et al. [10,11].

Fig. 2. Pressure dependence, p of ultrasonic speed, u in liquid $CF_3CF_2CHCl_2.$ (\longrightarrow), calculated by Eq. (2).

Fig. 3. Pressure dependence, p of ultrasonic speed, u in liquid $CCIF₂CF₂CHCIF.$ (- - - - - -), calculated by Eq. (2).

For each isotherm, the speed, u_s for the saturated liquid was estimated by extrapolation of the curves to the vapor pressure, p_s . The p_s values required in this calculation were derived from the equations reported Table 2

Experimental ultrasonic speed, $u/(m s^{-1})$ at various temperature, T/K and pressure, p/MPa in the liquid phase of $CF_3CF_2CHCl_2$ and CClF2CF2CHClF

p	$\boldsymbol{\mathcal{U}}$	\boldsymbol{p}	$\boldsymbol{\mathcal{U}}$	\boldsymbol{p}	\boldsymbol{u}	\boldsymbol{p}	$\boldsymbol{\mathcal{U}}$
$CF_3CF_2CHCl_2$							
283.15 K							
$0.0228^{\rm a}$	719.7 ^b	5.983	752.1	12.984	787.1	23.782	836.2
0.101	720.5	6.889	756.6	14.472	794.3	26.044	845.6
1.543	727.7	8.065	762.6	15.923	801.1	29.128	858.2
2.974	735.6	9.113	767.9	17.848	810.0		
4.205	742.1	10.046	772.8	19.371	816.9		
5.120	747.3	11.573	780.3	21.438	826.1		
293.15 K							
$0.0343^{\rm a}$	684.4^{b}	4.417	709.9	9.894	740.2	21.280	796.0
0.193	685.3	5.445	715.8	11.523	748.7	23.685	806.8
0.208	685.3	6.178	719.9	13.425	758.4	25.911	816.5
1.059	690.2	7.098	725.0	15.322	767.8	29.731	832.6
2.366	698.0	8.051	730.2	17.160	776.8		
3.257	703.9	9.053	735.7	19.048	785.7		
298.15 K							
0.0418^{a}	669.0^{b}	5.902	703.7	13.74	746.3	21.168	782.6
0.100	669.6	7.522	713.0	15.249	754.0	23.497	793.1
2.050	680.8	9.325	722.9	16.669	761.1	25.718	803.1
3.385	689.0	11.083	732.5	18.142	768.4	29.025	817.3
4.643	696.3	12.487	739.8	19.516	774.9		
303.15 K							
$0.0504^{\rm a}$	652.0^{b}	4.606	680.6	11.494	719.9	23.333	779.1
0.129	652.3	5.353	685.0	13.421	730.2	25.969	791.1
0.856	656.8	6.890	694.1	15.432	740.7	28.465	802.3
1.872	663.2	7.879	699.8	17.098	749.1		
2.994	670.4	8.673	704.3	18.908	758.0		
4.032	676.8	9.882	711.1	21.251	769.7		
313.15 K							
0.0722^a	620.2^b	5.003	652.0	12.076	694.5	21.155	742.3
0.100	620.3	6.142	659.3	13.435	702.1	23.074	751.7
1.002	626.2	7.042	667.1	14.772	709.4	25.671	764.0
1.929	631.9	6.142	659.3	16.445	718.3	28.486	776.8
3.306	641.0	8.963	676.3	18.006	726.5		
3.886	645.2	10.547	685.7	19.238	732.8		
323.15 K							
0.101 ^a	587.6 ^b	6.577			676.2		729.8
			631.8	13.702		23.788 25.985	
1.177	594.6	8.641	645.5	15.845	688.2		740.4
2.281	602.2	10.421	656.5	17.642	698.0	28.472	752.2
3.449	610.4	11.965	666.0	19.129	706.1		
5.171	622.7	12.420	668.6	21.283	717.2		
333.15 K							
0.139^{a}	554.6^{b}	4.307	586.2	11.632	636.8	19.444	
1.401	564.6	6.056	599.1	13.447	648.0	21.392	692.9
1.424	564.2	7.857	612.1	15.431	659.9	24.059	706.8
2.203	570.6	9.777	624.6	17.327	670.8		
343.15 K							
$0.1864 ^{\rm a}$	524.4 ^b	5.972	569.4	11.601	608.9	19.682	658.1
2.130	539.0	6.848	576.0	13.384	620.6	21.293	667.1
3.182	547.7	7.820	582.9	15.255	632.1	23.365	678.5
4.101	554.9	8.751	589.6	17.023	642.8	25.987	692.3
5.035	562.2	10.068	598.6	18.165	649.5	28.290	704.1

Table 2 (Continued)

Table 2 (Continued)

^{a,c} Vapor pressures, p_s derived from the equations in [3] and [4], respectively. b Ultrasonic speeds in the saturated liquid extrapolated to p_s .

by Widiatmo et al. [3] for $CF_3CF_2CHCl_2$ and Fukushima and Watanabe [4] for $CCIF₂CF₂CHCIF.$ The results of u_s , presented in Table 2 and plotted in Fig. 4, show nearly a linear dependence versus temperature, but that at 343.15 K shows a little higher value from the linear curve in both liquids. The sample, which filled up at room temperature into a sample chamber of closed system (Fig. 1), was probably compressed by the thermal expansion with increasing temperature, and therefore the value of u near the saturation pressure at 343.15 K was due to shift to that at higher pressure compared with the gauge pressures. Moreover, close to the critical temperature the uncertainty in the experimental u sharply increased with greater absorption of the acoustic wave excited in the sample, and measurement near the saturation region became

impossible. The results of u_s except that at 343.15 K are represented by the following equation

$$
u_{\rm s}/(\text{m s}^{-1}) = \sum_{i=0}^{2} a_i (T/\text{K} - 298.15)^i \tag{1}
$$

The values of the coefficients a_i are listed in Table 3.

In a previous work [1] the authors have reported that the values of u in various organic liquids at constant temperature show a linear relation with density, except those in the critical region. The densities for the compounds investigated here have been measured by Tanaka et al. at the saturated liquid [6] and at 298.15 K and 323.15 K and at pressures up to 78 MPa [12]. As illustrated in Fig. 5, the relationships between ultrasonic speeds and densities also indicated the

Fig. 4. Temperature dependence, T of ultrasonic speed u_s in the saturated liquid (\bigcirc), CF₃CF₂CHCl₂; (\bigtriangleup), CClF₂CF₂CHCIF; (\blacktriangle), $CF_3CF_2CH_2OH$; (\bullet), CCl_2FCCIF_2 (\bullet), calculated by Eq. (1).

Fig. 5. Density dependence, ρ of ultrasonic speed, u corresponding to the whole pressure ranges. (\bigcirc \Box): CF₃CF₂CHCl₂; (\bullet \Box): CClF₂CF₂CHClF; (○●): 298.15 K; (□■): 323.15 K.

Table 3

The coefficients, a_i , b_i of equations Eqs. (1) and (2) and mean deviation, δ_{mean}

Compound	$CF_3CF_2CHCl_2$	CCIF2CF2CHCIF
Ultrasonic speed in the saturated liquid		
a ₀	668.78	688.16
a_1	-3.324	-3.448
a ₂	2.442×10^{-3}	6.591×10^{-3}
B for the Tait equation, $C=0.2362$		
b_0	24.919	27.085
b ₁	-0.2919	-0.2889
b ₂	9.991×10^{-4}	6.258×10^{-4}
δ_{mean} (283.15~333.15 K)	0.065	0.048
n	138	155

 $\delta_{\text{mean}} = \Sigma |100(u_{\text{exn}}-u_{\text{calc}})/u_{\text{calc}}|/n$, where *n* is the number of data points.

linear relation, and therefore they were well represented by the Tait equation, which is usually used to correlate compressed liquid densities [13].

$$
\frac{1/u_{\rm p}}{1/u_{\rm s}} = 1 - C \ln \left[\frac{(B+p)}{(B+p_{\rm s})} \right]
$$
 (2)

Where, u_p and u_s are respectively, the ultrasonic speeds at pressure p and along the saturated line obtained by extrapolation of u_p to the saturated pressure p_s . From the experimental data at each isotherm, the coefficients, C and B were calculated by the leastsquares analysis using the Marquardt method [14]. In this work, the value of C was fixed at 0.2362 as the average values for both substances. B was also evaluated as a function of temperature by Eq. (3) except that at 343.15 K and the coefficients, b_i are listed in Table 3 with mean deviation.

$$
B/\text{MPa} = \sum_{i=0}^{2} b_i (T/\text{K} - 298.15)^i \tag{3}
$$

The ultrasonic speeds, calculated by the Tait equation with the coefficients of Eqs. (1) and (3) , reproduce well the experimental values with a maximum deviation of $\pm 0.25\%$ for CF₃CF₂CHCl₂, and $\pm 0.20\%$ for $CCIF_2CF_2CHCIF$, respectively. But the results at 343.15 K deviated at $0.5 \sim 0.7\%$ from the calculated values in both fluids (see Fig. 6).

For these compounds, the absolute u in $CF₃CF₂CHCl₂$ has a lower value by about 20 m s⁻¹ than the one in $CCIF₂CF₂CHCIF$ under all corre-

Fig. 6. Deviation plot of experimental ultrasonic speed u_{exp} from the calculated value $u_{\text{calc.}}$ (\triangle): 283.15 K; (\Box): 293.15 K; (\bullet) 298.15 K; (∇) : 303.15 K; (\diamond) : 313.15 K; $(+)$ 323.15 K; (\times) : 333.15 K; (A) 343.15 K.

sponding conditions. This behavior can be interpreted qualitatively by the differences in molecular structure based on the Eyring liquid free volume model [1] It shows larger speed in molecular fluids having smaller intermolecular free volume, V_f in general. The van der Waals radius of H atom is nearly the same as that of F atom, but the radius of Cl atom is larger than those of the other two atoms. The substance, $CCIF₂CF₂CHCIF$, which has a symmetrical molecular structure, is expected to pack more closely under these conditions. Then, the speed u in $CF₃CF₂CHCl₂$, which has a large free volume, should have lower absolute u value as confirmed experimentally. This consideration is also supported qualitatively from the difference of isothermal compressibility, κ_T and isentropic compressibility, $\kappa_S = [1/(\rho u^2)]$, where ρ is the density] in between both substances. That is, the absolute values of $\kappa_{\rm T}$ and $\kappa_{\rm S}$ for $CCIF_2CF_2CHCIF$ are lower than those for the later one, as is illustrated in Fig. 7, and they decrease having low pressure dependence with increasing pressure. The densities required for estimating the values of $\kappa_{\rm T}$ and $\kappa_{\rm S}$ were derived from PVT data reported by Tanaka et al. [6].

In the precision industry, the compounds investigated are used as solvents for ultrasonic cleaning.

Fig. 7. Pressure dependence, p of isothermal compressibility, κ ^T and isentropic compressibility κ_S in the liquid phase. ($\bullet \blacksquare \blacktriangle \blacktriangledown$) κ_{T} ; ($\odot \Box \triangle \triangledown$) κ_{S} : ($\odot \Box \bullet \blacksquare$) CF₃CF₂CHCl₂; ($\triangle \triangledown \blacktriangle \blacktriangledown$): CCIF₂CF₂CHCIF; ($\bigcirc \Delta \triangle$): 298.15 K; ($\blacksquare \blacksquare \blacktriangledown$) 323.15 K.

Acoustic wave excited in the sample is absorbed by the viscosity, η , thermal conductivity, λ and thermal radiation, I . Among these properties, the value of I is extremely small in general compared with those for other two contents, and the classical absorption of acoustic wave, ζ/f^2 [15] is given by

$$
\zeta/f^2 = \frac{2\pi^2}{\rho u^3} \left(\frac{4}{3}\eta + \frac{\gamma - 1}{C_{\mathbf{p}}} \lambda\right)
$$
 (4)

Where C_p is the isobaric specific heat capacity, and γ is the ratio of specific heat capacities. Ultrasonic speeds in the liquid phase of $CF_3CF_2CHCl_2$, and $CCIF₂CF₂CHCIF$ show comparatively lower values than those observed in alcohol, $CF₃CF₂CH₂OH$, because they are higher than those of CCl_2FCClF_2 as shown in Fig. 4. Where the ultrasonic speeds and other properties for CCl_2FCClF_2 were derived thermodynamically from PVT data and several values [2]. When it was supposed that the frequency excited in sample liquid was constant, the absorption, ζ/f^2 calculated by Eq. (4) for these compounds show a small value rather than those for CCl_2FCClF_2 and $CF₃CF₂CH₂OH$ as also listed in Table 1. These facts

suggest that it will be possible to achieve large acoustic energy in the compounds investigated here.

4. Conclusion

The ultrasonic speeds in the liquid phase of $CF₃CF₂CHCl₂$ and $CCIF₂CF₂CHClF$, which have been developed as a new cleaning agents, were measured at temperature from 283 to 343 K and pressures up to 30 MPa with an uncertainty within $\pm 0.2\%$. It is found that these results were represented well by the Tait equation in the whole temperature and pressure ranges. These compounds are used as cleaning agents in the precision industry. The low ultrasonic speeds in liquid phase corresponding to a small attenuation constant of acoustic wave, ζ/f^2 were observed for these propane-based compounds. From these facts, it is found that these substances, showing lower ultrasonic speed similar to those in CCl_2FCClF_2 and $CF₃CF₂CH₂OH$, have excellent characteristics of cleaning agents.

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