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Ultrasonic Speed in Mixtures of Monochlorodifluoromethane and Monochloropentafluoroethane Under High Pressures[1]

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The ultrasonic speed u of $[(1-x)\,\mathrm{CHClF_2}(l)+x\mathrm{C_2ClF_5}(l)]$ including the azeotropic mixture $[\mathrm{CHClF_2}(l)+\mathrm{C_2ClF_5}(l)]$ was measured at pressures up to 51 MPa within the temperature range 283.15 to 373.15 K, using a sing-around technique operated at a frequency of 2 MHz with an estimated uncertainty of less that $\pm 2.4\ \mathrm{m\cdot s^{-1}}$. For $x=0.1537$ and 0.6268, measurements of the vapor pressure are also reported.

KEY WORDS: binary mixture; critical region; high pressure; R22; R502; R115; refrigerants; ultrasonics.

1. INTRODUCTION

The variation of the adiabatic compressibility κ_S for fluids with temperature and pressure is an important thermodynamic property, which can be obtained from measurements of the speed of sound u and the density ρ by use of the equation

$$\kappa_S = 1/\rho u^2 \tag{1}$$

Until recently, this method has not been extensively exploited for fluorocarbon refrigerants at high pressures.

In our earlier work, the "ultrasonic" speed u determined in the mixtures $[(1-x)\,\mathrm{CHClF_2}(l)+x\mathrm{C_2ClF_5}(l)]$ [1], including the azeotrope

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$[\mathrm{CHClF_2}(I) + \mathrm{C_2ClF_5}(I)]$, was measured between 283.15 and 323.15 K at pressures up to 50 MPa [1, 2]. The measurements reported here extend the temperature range to 373.15 K and include mole fractions of 0.1537 and 0.6268; the azeotropic mixture, $x = 0.3700$, is commonly known as R502. The $u(T, p)$ results for u as a function of the temperature T and pressure p are discussed together with those obtained previously [1].

2. EXPERIMENTAL

The liquids used were supplied by Daikin Kogyo Co; the purities were determined by glc and found to be better than 99.9 mol %. The mixture compositions were determined by weighing, and the uncertainty of the mole fractions was better than ±0.0006.

Ultrasonic speeds were measured by a sing-around technique with a fixed path-length interferometer operated at a frequency of 2 MHz similar to that described previously [3]. Since the apparatus was designed primarily for operation at considerably high pressures, two minor modifications were implemented for the pressure range encountered here. First, the pressure, which was generated by a hand oil pump, was transmitted to the sample by a piston-cylinder separator, which was immersed in a stirred fluid bath controlled within ±0.02 K with the interferometer. Below 10 MPa, the pressure was determined using a strain gauge (Nagano Keiki Ltd. Model KH-15) with a resolution of 1 kPa. The maximum error in the pressure measurements above 10 MPa was ±0.08 MPa. The uncertainty in the ultrasonic speed was estimated to be no greater than $\pm 1.8\ \mathrm{m \cdot s^{-1}}$ at pressures below 8 MPa, while at higher pressures the uncertainty approached $\pm 2.4\ \mathrm{m \cdot s^{-1}}$, which includes the variation in the cell path length.

The vapor pressures p^{l+g} for $[(1-x)\,\mathrm{CHClF_2} + x\mathrm{C_2ClF_5}]$ with $x = 0.1537$ and 0.6268 were determined using a constant-volume static technique between 298.15 and 353.15 K, with an uncertainty of 50 Pa or 5 mK.

3. RESULTS AND DISCUSSION

Table I lists values of the ultrasonic speed u as a function of p in five different compositions of $[(1-x)\,\mathrm{CHClF_2} + x\mathrm{C_2ClF_5}]$ at temperatures between 283.15 and 373.15 K. The experimental results for pure and azeotropic fluids supplement our previous measurements between 283.15 and 323.15 K [1].

The present interferometer is restricted to fluids with u smaller than $180\ \mathrm{m \cdot s^{-1}}$, an artifact which conspired with the known effects of absorp-

Table I. Ultrasonic Speed u in $[(1-x)\,CHClF_2 + xC_2ClF_5]$ for Various Compositions x at Temperatures T and Pressures p

p (MPa)	u ($m \cdot s^{-1}$)	p (MPa)	u ($m \cdot s^{-1}$)	p (MPa)	u ($m \cdot s^{-1}$)	p (MPa)	u ($m \cdot s^{-1}$)
$x = 0$ ($CHClF_2$)							
333.15 K							
2.44	376.9	3.31	397.5	18.9	587.5	39.2	721.9
2.95	389.5	6.07	447.0	23.8	625.1	44.6	750.0
		9.17	489.0	29.0	661.6	50.0	777.3
		13.7	540.0	34.4	695.2		
343.15 K							
3.56	337.6	6.50	402.0	19.6	558.3	36.8	679.5
4.69	365.9	8.92	441.0	23.1	587.4	41.7	707.5
		10.5	462.4	27.4	619.5	46.0	730.4
		15.9	524.3	31.8	649.1	51.4	736.6
353.15 K							
5.53	323.1	7.70	369.2	21.7	545.0	39.4	666.9
6.65	350.5	9.16	398.3	26.3	580.3	44.0	693.0
		16.2	492.2	30.1	608.1	50.0	723.4
		18.4	513.5	33.9	633.6		
363.15 K[a]							
5.02	236.3	8.36	338.8	21.5	514.3	41.1	656.9
7.98	330.4	11.2	392.7	25.7	550.6	45.0	678.7
		13.4	424.7	31.4	594.5	50.2	706.2
		18.3	482.5	35.2	620.0		
369.15 K							
5.83	266.4	8.27	310.2	15.4	430.5	40.0	643.5
7.25	281.6	9.12	331.0	19.9	487.0	44.2	669.0
		10.5	359.9	24.8	531.7	50.7	704.0
		12.7	397.1	34.9	609.7		
373.15 K							
7.97	281.2	10.2	337.2	21.9	500.1	40.0	640.6
8.47	296.8	12.3	378.4	24.9	527.5	44.5	667.6
		15.9	431.5	30.3	572.6	50.0	698.6
		18.9	467.3	35.2	608.7		

[a] Critical temperature T_c.

Table I. *(Continued)*

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 ($\mathrm{m \cdot s^{-1}}$)
			$x = 0.1573$				
			283.15 K				
0.88	552.3	3.13	575.3	16.0	676.1	33.0	775.3
1.25	556.1	5.02	593.3	19.2	698.6	38.6	801.7
		8.45	622.4	22.4	718.1	44.0	826.2
		10.6	639.5	27.9	749.3	49.0	847.2
			293.15 K				
0.98	500.7	3.47	531.4	14.2	628.0	33.8	749.4
1.64	509.6	5.10	548.9	18.9	661.3	38.8	774.5
		8.63	583.3	23.9	693.5	44.2	799.8
		11.3	605.1	28.9	722.4	49.6	823.3
			298.15 K				
1.13	476.4	2.55	496.6	14.5	614.1	34.1	737.9
1.70	485.3	6.31	540.0	18.8	645.7	39.3	764.2
		7.93	556.5	23.7	677.8	44.1	787.2
		11.1	586.1	29.2	710.7	49.0	809.1
			303.15 K				
1.28	452.4	2.32	468.8	14.5	595.5	34.3	723.3
1.64	458.8	4.34	495.8	19.1	630.4	38.7	746.7
		7.24	528.9	23.8	662.2	43.8	771.4
		9.68	553.1	29.5	697.0	49.1	795.4
			313.15 K				
1.58	400.9	4.30	447.3	14.3	558.2	33.8	692.4
2.22	412.8	5.91	469.6	19.7	602.0	38.7	718.9
		9.50	511.8	24.3	633.8	44.0	746.2
		11.6	533.6	29.5	666.8	50.1	774.2
			323.15 K				
2.04	348.8	3.98	391.2	14.3	552.8	34.2	667.8
2.52	361.3	4.96	408.6	20.1	572.3	39.3	696.4
		6.65	434.7	24.2	603.0	44.1	720.8
		9.89	475.5	29.1	636.5	50.8	753.9
			333.15 K				
2.61	295.9	4.37	348.2	14.6	491.6	34.0	640.9
3.41	323.6	6.25	383.9	18.9	532.1	39.4	672.5
		9.68	434.6	23.9	572.6	44.1	697.0
		11.8	461.1	28.9	608.4	49.7	725.0

Table I. *(Continued)*

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 $(\mathrm{m \cdot s^{-1}})$
343.15 K							
3.63	262.6	4.60	295.1	14.5	456.7	33.4	611.8
3.94	274.1	5.59	321.2	18.6	499.1	38.8	644.6
		7.52	359.7	23.5	541.4	43.6	671.0
		11.7	423.2	28.4	578.2	51.1	709.4
353.15 K							
4.73	230.2	8.06	324.9	17.2	453.8	34.0	591.3
5.60	262.9	9.82	356.9	19.7	480.2	39.2	623.9
		11.3	381.7	24.0	517.9	43.9	651.0
		13.9	416.0	28.5	553.5	50.7	686.8
363.15 K							
5.40	191.9	7.59	272.6	15.1	402.5	34.2	570.7
6.45	237.9	8.24	287.7	18.5	441.2	40.6	611.2
		9.72	319.8	23.1	485.6	44.1	631.8
		10.8	339.6	30.4	543.9	50.1	663.7
373.15 K							
6.66	186.1	8.19	241.0	20.4	434.1	34.8	553.2
7.23	209.2	9.96	284.6	22.9	458.0	39.5	583.7
		14.0	355.1	25.3	479.9	44.6	614.0
		17.7	403.5	29.6	515.2	50.0	643.6
$x = 0.3700$ (azeotropic mixture)							
333.15 K							
2.98	273.9	3.30	284.3	17.9	494.3	29.6	583.9
3.13	278.1	4.65	319.9	19.3	506.0	36.2	621.5
		7.02	361.1	22.2	530.7	41.3	654.0
		9.69	401.4	26.2	560.6	49.2	693.7
343.15 K							
3.75	218.7	6.25	302.4	14.5	427.3	33.6	585.8
4.73	262.8	7.48	325.8	20.2	485.1	38.7	616.7
		8.92	349.8	24.6	522.0	43.4	643.0
		12.7	405.3	29.7	560.0	49.0	670.6
353.15 K							
5.45	229.7	7.65	287.7	21.8	473.5	34.1	565.9
6.20	253.7	9.05	316.4	25.5	503.9	38.5	593.8
		11.9	362.5	28.9	530.2	44.6	628.5
		15.0	402.9	32.9	558.0	48.8	650.4

Table I. *(Continued)*

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 ($\mathrm{m \cdot s^{-1}}$)
355.35 K[a]							
5.02	193.5	7.84	282.8	19.6	447.2	37.9	585.5
6.42	245.9	9.34	313.6	24.8	493.5	46.9	637.4
		12.8	369.5	29.5	529.6		
		15.7	406.2	34.1	561.7		
363.15 K							
6.15	196.0	10.2	302.5	22.7	456.4	39.1	576.6
7.87	251.6	12.6	341.6	27.9	500.3	42.1	594.9
		17.2	401.6	30.9	522.2	46.6	620.0
		20.7	438.4	34.8	549.4	50.0	637.7
373.15 K							
7.94	214.0	11.3	291.3	24.7	452.7	40.6	567.1
8.68	234.1	15.0	348.0	29.6	492.3	45.9	597.8
		19.5	401.6	33.8	523.1	50.8	623.7
		22.4	431.6	37.8	549.8		
$x = 0.6268$							
283.15 K							
0.97	459.9	2.58	480.4	23.1	646.7	41.9	746.3
1.63	468.8	7.89	534.7	27.1	670.5	46.4	765.9
		11.2	561.6	30.9	691.9	50.7	784.4
		16.0	600.0	34.9	712.3		
293.15 K							
1.08	413.1	5.65	474.8	19.3	592.0	38.9	706.6
2.47	435.6	7.61	494.4	24.3	625.2	43.8	730.3
		10.7	524.3	29.7	657.9	47.7	748.2
		15.1	560.8	34.9	686.2	51.0	762.2
298.15 K							
2.21	409.3	5.98	459.4	21.1	590.2	36.7	683.4
3.46	427.7	6.13	461.0	24.6	614.0	40.9	704.3
		8.66	487.5	28.3	636.6	45.2	725.0
		12.5	524.6	32.4	660.2	50.4	748.6
303.15 K							
2.63	387.2	5.54	428.9	20.5	568.1	37.6	674.3
3.72	403.9	7.28	449.1	25.2	600.0	39.7	684.8
		9.42	472.7	32.3	645.7	43.8	704.8
		14.1	517.6	34.6	658.0	47.9	724.6

Table I. *(Continued)*

p (MPa)	u ($m \cdot s^{-1}$)	p (MPa)	u ($m \cdot s^{-1}$)	p (MPa)	u ($m \cdot s^{-1}$)	p (MPa)	u ($m \cdot s^{-1}$)
313.15 K							
2.77	344.8	4.66	378.2	14.9	495.6	35.8	640.4
3.49	358.5	5.60	392.7	19.3	532.7	40.5	665.6
		8.17	425.3	26.6	584.8	44.7	686.9
		10.9	456.8	29.7	604.3	50.9	715.5
323.15 K							
3.06	294.3	5.64	347.3	12.4	435.7	33.0	600.1
3.78	311.6	7.30	371.7	15.9	470.5	37.8	627.5
		8.98	395.3	20.1	507.0	43.1	655.7
		10.6	416.4	22.3	528.0	49.4	686.5
333.15 K							
3.16	242.2	5.30	300.3	13.2	418.4	34.5	587.1
3.90	265.9	6.15	316.9	21.3	495.0	39.1	613.7
		9.90	376.4	25.4	526.9	44.4	641.6
		11.1	394.0	30.2	559.9	51.5	677.0
343.15 K							
3.29	182.2	4.52	230.1	14.6	403.2	42.2	588.6
3.55	190.7	5.90	268.5	21.0	465.5	44.3	619.5
		7.32	297.5	26.2	506.7	50.0	648.6
		10.1	343.0	31.8	545.8		
353.15 K							
4.49	171.5	6.00	229.2	15.2	385.9	33.9	541.7
5.44	211.7	7.69	270.6	19.8	432.6	39.2	574.3
		10.1	315.5	23.9	469.0	44.2	602.1
		12.3	349.2	28.7	506.2	50.0	632.2
363.15 K							
6.96	214.7	9.37	271.2	24.8	455.6	45.1	590.3
7.82	237.4	11.5	309.0	30.6	500.3	49.9	615.3
		14.5	351.4	34.8	529.3		
		19.9	411.0	40.0	561.4		
373.15 K							
7.00	179.0	8.80	216.7	17.4	362.5	34.5	508.6
7.70	187.3	9.98	253.7	21.7	407.6	39.9	542.5
		12.5	297.6	25.7	442.5	44.4	568.6
		14.6	328.2	30.7	482.1	49.7	597.0

Table I. *(Continued)*

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 ($\mathrm{m \cdot s^{-1}}$)
$x = 1(C_2ClF_5)$							
333.15 K							
2.85	225.4	4.62	273.1	19.8	459.5	40.8	596.5
3.63	248.0	7.63	327.7	25.4	502.8	46.2	624.1
		10.9	371.3	31.3	540.8	51.4	648.8
		15.2	417.5	35.6	567.6		
343.15 K							
2.82	172.5	4.85	244.3	15.6	401.8	33.2	538.2
3.71	210.4	5.63	263.1	20.7	449.7	39.9	577.6
		6.71	285.1	24.8	482.1	46.1	610.1
		9.85	333.6	30.5	524.1	50.0	629.7
353.15 K[a]							
4.06	171.8	5.25	213.7	14.5	366.6	34.5	528.5
4.24	179.2	7.28	262.4	20.2	424.2	40.1	561.9
		9.42	298.1	24.4	458.7	44.0	582.5
		11.8	333.4	29.5	496.1	50.4	613.4
363.15 K							
5.73	191.0	7.97	243.7	20.2	402.1	34.7	512.0
6.95	220.6	10.3	286.2	22.7	424.5	40.9	548.7
		11.9	310.0	25.8	450.0	45.4	573.1
		15.3	353.2	30.9	488.1	50.8	600.7
373.15 K							
6.43	178.6	8.10	218.6	19.5	377.7	34.3	493.3
7.67	211.5	10.3	261.5	22.3	403.5	39.6	526.4
		11.7	285.0	25.1	426.6	45.3	558.2
		15.2	331.1	29.4	459.4	50.3	583.5

tion to hinder measurements at pressures close to p^{l+g}. The results reported here are in excellent agreement with values obtained elsewhere [4].

Since these fluids are considered stratospherically safe, their thermodynamical properties are important to the refrigeration industry. Consequently, comparisons have been made between the experimental quantity and estimates of $u(T, p, x)$ obtained from various empirical equations of state applicable to refrigerants. Estimates calculated from equations of state reported elsewhere [5, 6] differ considerably from our present values.

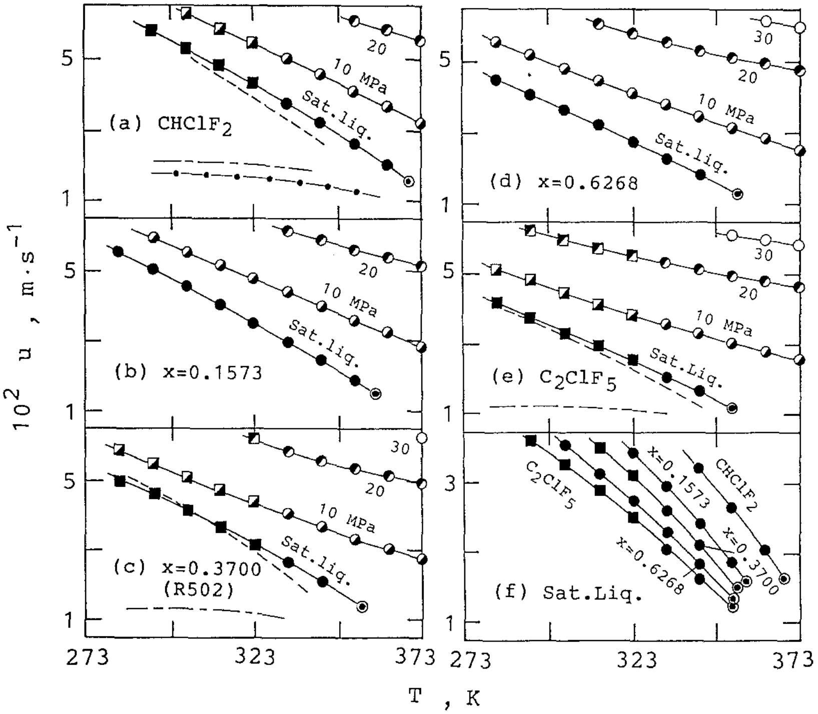

Fig. 1. Temperature dependence of ultrasonic speed u in the liquid phase of $[(1-x)\,\mathrm{CHClF_2}+x\mathrm{C_2ClF_5}]$. (○) This work; (□) Refs. 1 and 2; (—·—) saturated gas [10]; (----) and (——) estimated value for saturated liquid and gas; (⊙) critical point.

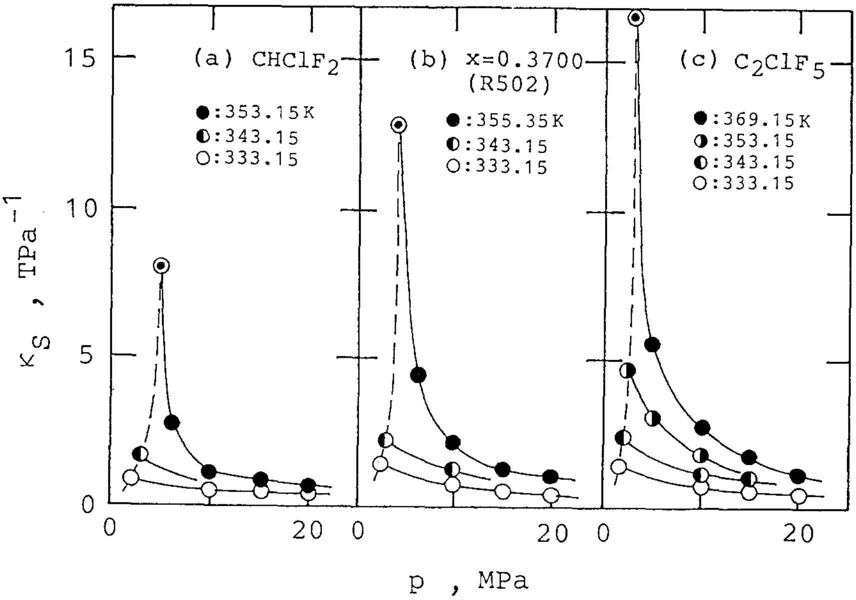

Fig. 2. Pressure dependence of isentropic compressibility κ_S in the liquid phase of $[(1-x)\,\mathrm{CHClF_2}+x\mathrm{C_2ClF_5}]$ near the critical region. (----) Saturation line; (⊙) critical point.

Table II. Values of p^{l+g} Determined for $[(1-x)\mathrm{CHClF_2} + x\mathrm{C_2ClF_5}]$ with Mole Fractions of 0.1537 and 0.6268 at Temperatures T

T (K)	p^{l+g} (MPa) $x = 0.1537$	$x = 0.6268$
298.15	1.119	1.124
303.15	1.274	1.262
313.15	1.634	1.607
323.15	2.056	2.002
333.15	2.557	2.473
343.15	3.143	3.021
348.15	3.475	3.342
353.15	3.830	3.681

The values of u in the saturated liquid and gas are estimated from pVT data in Refs. 7–9 for $[(1-x)\,\mathrm{CHClF_2} + \mathrm{xC_2ClF_5}]$, including the pure fluids, and are indicated in Fig. 1 with the experimental speeds. In general, at the lower temperatures the agreement is fair, while at the higher temperatures the differences are more prounced.

The composition dependence of $u(T)$ is shown in Fig. 1f and can be explained in terms of the polarity of $\mathrm{CHClF_2}$, which is greater than that of $\mathrm{C_2ClF_5}$ [11]. Estimates of the adiabatic compressibility κ_S have been obtained from Eq. (1) using the mass density obtained from the literature [7–9, 12]. Figure 2 shows the pressure dependence of κ_S, which, close to the critical point, is as expected.

Table III. Values of p_c and T_c for $[(1-x)\mathrm{CHClF_2} + x\mathrm{C_2ClF_5}]$ with Mole Fractions of 0.1573 and 0.6268, Determined by Graphical Analysis of the Results Reported in Table II Combined with Critical Values for the Pure and Azeotropic Fluids from the Literature [8], and the Speeds at Critical Point, u_c

x	p_c (MPa)	T_c (K)	$u_c{}^a$ ($\mathrm{m \cdot s^{-1}}$)
0 ($\mathrm{CHClF_2}$)	4.98	369.15	167.3
0.1573	4.53	359.63	153.2
0.3700 (R502)	4.07	355.35	146.7
0.6268	3.62	353.60	128.0
1 ($\mathrm{C_2ClF_5}$)	3.15	353.15	118.7

[a] Value obtained by extrapolation to critical point from the experimental speeds in Table I.

The vapor pressures of $[(1-x)\,\mathrm{CHClF_2} + x\mathrm{C_2ClF_5}]$ with mole fractions $x = 0.1573$ and 0.6268 are listed in Table II. These values were combined with the vapor pressure for the pure fluids [8], to provide estimates of the critical temperature and pressure, which are reported in Table III.

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