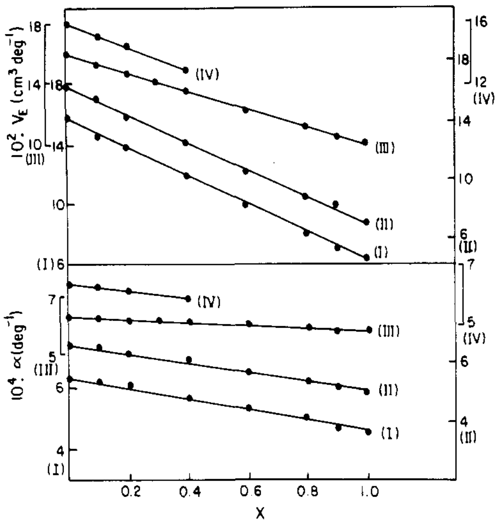

Figure 2. Composition variation of thermal expansion coefficient (α) and molar expansivity (V_E) of $Fe(NO_3)_3 \cdot 9.08H_2O + M(NO_3)_2 \cdot RH_2O$ systems at 300 K. Scales on the Y axis are (I) for Ca, (II) for Cd, (III) for Zn, and (IV) for Mg.

with Mg^{2+} ions resulting in a decrease of $\bar{V}(Mg(NO_3)_2 \cdot 6H_2O)$ as observed.

Both the expansion coefficient ($\alpha = -(1/\rho)(d\rho/dT)$) and the molar thermal expansivity ($V_E = dV/dT$) of the mixtures show a decrease (Figure 2) on addition of hydrated M^{2+} to $Fe(NO_3)_3 \cdot 9H_2O$. Sharma et al. (*8*) have shown that V_E could be approximated to the product of α and V_0. The addition of hydrated M^{2+} decreases the number of moles of NO_3^- ions from 3 to 2 per mole of the mixture. Also, the moles of water associated with the cations decrease from 9 to 4 or 6 per mole of the mixture. Both these factors would lead to a decrease in V_0 and hence in V_E, as observed.

Variation in α is opposite to that expected from the Born model of ion-water interactions. Inove et al. have shown (*12*) that a decrease in water content changes the hydration number of Fe^{3+} ion from 6 to 4 and results in ion-pair formation displacing coordinate water into lattice water which has high configurational contribution to α (*13*). It may be concluded that the addition of divalent cations results in a greater electrostriction to lattice water and a decrease in α, as observed.

Registry No. $Fe(NO_3)_3 \cdot 9H_2O$, 7782-61-8; $Ca(NO_3)_2 \cdot 4H_2O$, 13477-34-4; $Cd(NO_3)_2 \cdot 4H_2O$, 10022-68-1; $Zn(NO_3)_2 \cdot 6H_2O$, 10196-18-6; $Mg(NO_3)_2 \cdot 6H_2O$, 13446-18-9.

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Ultrasonic Speed in Liquid Phase of Bromotrifluoromethane (R13B1) under High Pressures

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The ultrasonic speeds in the liquid phase of bromotrifluoromethane (R13B1) were measured at temperatures from 283.15 to 323.15 K and pressures from near saturated vapor pressure to about 50 MPa by using a sing-around technique operated at a frequency of 2 MHz. The ultrasonic speeds show a large pressure effect in the lower pressure region as the temperature comes close to critical. The smoothing curve for the experimental values fits well to the observed values in high-pressure range. However, in the vicinity of vapor pressure, acoustic absorption in the liquid phase was observed which induced distortion in speed; so the present results in this region have large deviations from the fitting curve.

Introduction

Experimental work on ultrasonic speed for refrigerants are rare, especially at high pressure. In our recent work (*1*), a new apparatus was constructed using a sing-around technique employing a fixed-path ultrasonic interferometer of 2 MHz, which was used to observe the precise ultrasonic speed in liquid under high pressure. The speed in the liquid phase of dichlorotetrafluoroethane (R114) was measured at various conditions of temperature and pressure. Kokernak and Feldman (*2*) measured the ultrasonic speed in liquid of dichlorodifluoromethane (R12) under its saturated vapor pressure, and estimated the values of some refrigerants including R114 by a theoretical rule. This report is the only one concerning study of the speed in the liquid phase of refrigerant R114. However, the value of R114 reported in their paper was ascertained to differ about 15% from that obtained by extrapolation of our experimental results (*1*) to the saturation vapor pressure. In this paper, the ultrasonic speed in the liquid phase of bromotrifluoromethane (R13B1) was measured at temperatures from 283.15 to 323.15 K, at pressures from near saturation to about 50 MPa. Temperature and pressure effects on sound speed are discussed and compared with those for refrigerant R114 reported previously.

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Table I. Ultrasonic Speed $u/(\mathrm{m \bullet s^{-1}})$ in the Liquid Phase of Bromotrifluoromethane (R13B1) at Several Pressures p/MPa

p	u	p	u	p	u
283.15 K					
1.107[a]	367.3[b]	6.75	423.9	23.60	543.4
1.39	370.4	10.28	456.7	29.09	572.0
1.52	371.2	11.81	468.2	32.83	590.0
1.66	373.2	13.76	482.1	39.90	621.3
2.47	383.1	16.84	503.2	44.99	642.1
3.53	395.2	19.66	520.8	46.68	649.1
4.60	406.4	23.39	542.2	51.19	666.3
293.15 K					
1.428[a]	326.1[b]	13.22	450.3	39.16	597.2
1.80	331.2	15.66	467.5	42.16	610.5
2.78	345.5	18.55	487.6	45.94	626.0
4.10	360.8	21.50	506.1	49.40	639.9
5.77	381.7	25.69	530.7	50.13	642.7
7.90	403.8	30.77	557.5	52.07	649.9
9.97	424.5	33.87	572.9		
298.15 K					
1.612[a]	309.1[b]	9.41	401.7	32.75	555.9
2.76	324.4	12.24	424.5	36.72	575.0
2.78	324.8	15.20	450.5	40.59	592.5
3.32	332.4	19.00	475.9	44.00	607.4
3.96	339.6	23.11	503.6	46.67	618.4
5.58	361.1	26.77	524.6	49.77	630.8
7.60	383.6	29.69	540.4	51.03	635.8
303.15 K					
1.814[a]	290.0[b]	14.15	429.5	39.06	576.5
3.37	311.1	17.47	454.7	43.37	595.8
4.65	331.0	20.78	476.5	47.27	612.0
6.28	352.3	24.59	501.3	48.44	617.1
8.88	381.3	28.80	525.3	50.94	626.7
9.87	389.7	32.62	545.1		
12.43	414.1	36.44	564.3		
313.15 K					
2.273[a]	258.5[b]	14.51	405.4	36.79	545.9
6.75	322.5	17.55	430.1	39.78	560.0
7.89	337.5	21.47	458.3	42.30	570.8
10.04	362.4	24.83	480.2	45.80	587.3
11.40	376.8	28.46	502.0	49.28	601.8
12.81	390.4	32.42	523.5	52.44	614.5
323.15 K					
2.915[a]	223.5[b]	20.68	428.8	44.40	562.7
8.79	316.1	24.29	454.6	46.56	572.1
10.81	341.1	29.13	484.6	50.66	589.6
12.59	360.2	32.36	503.0	50.69	589.7
14.53	378.6	37.96	532.1		
17.50	404.7	41.35	548.5		

[a] Saturated vapor pressure p_s. [b] Ultrasonic speed at p_s.

Experimental Section

Bromotrifluoromethane $\mathrm{CBrF_3}$ (R13B1) was supplied by Daikin Kogyo Co., and its purity was better than 99.9%.

The method used for measurement of ultrasonic speed was a sing-around technique with fixed-path ultrasonic interferometer at a frequency of 2 MHz employing gated amplifier, and was similar to that described previously (*1*). The reliability of this apparatus was confirmed by measuring the speed in pure benzene, in which the precise values of ultrasonic speed are known (*3*, *4*). The maximum uncertainty was 1.8 m·s^{-1} (0.2%) over the ranges of present experimental conditions (*1*). The vapor pressure for refrigerant R13B1 is 1.61 MPa at 298.15 K (*5*). The sample was charged after the sample chamber was held for a long time at lower temperatures and in a vacuum.

Results and Discussion

The experimental ultrasonic speeds u in the liquid phase of bromotrifluoromethane (R13B1) at various temperatures T and pressures p are listed in Table I, and are illustrated graphically as a function of pressure in Figure 1. From this figure, the speeds in the present fluid are presumed to have values lower than 300 m·s^{-1} at high temperature. In this work, the speed u ($=2L/t$) was obtained by measuring the period t which can be measured when a short acoustic pulse travels over a known distance L in the sample. It is well-known that the distortion of the acoustic wave occurs in the vicinity of the transducer (*6*). Moreover, experiments using short-path interferometer showed increased uncertainty on observed ultrasonic speed. And so, in the present apparatus, the distance L between transducer and refractor is chosen as 15.123 ± 0.0016 mm from considerations of observed error. On the other hand, when the acoustic wave returned from the reflector to transducer, the gated amplifier was opened electrically, and the reflected signal was detected by the same transducer. The gate time used for this measurement was from 30 to 100 μs. Thus a speed lower than 300 m·s^{-1} was not observable with the fixed-path interferometer described above.

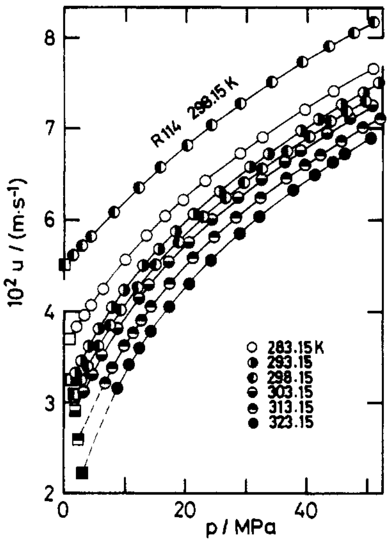

Figure 1. Pressure dependence of ultrasonic speeds u in the liquid phase of regrigerant R13B1: ○, experimental values; ☐, derived values at saturated vapor pressure.

Table II. Coefficients a_i for Eq 1 and Root-Mean-Square Deviation δ_{RMS}

T/K	a_0	a_1	$-a_2$	10^3a_3	-10^6a_4	δ_{RMS},[a] %
283.15	355.39	12.0809	0.2525	3.9678	2.5888	0.16
293.15	307.26	14.8576	0.3815	6.7589	4.7756	0.17
298.15	287.08	15.1517	0.3729	6.3511	4.3867	0.19
303.15	262.12	16.8767	0.4574	8.2496	5.9297	0.20
313.15	221.93	17.9534	0.4601	7.5673	4.9601	0.11
323.15	164.66	22.4130	0.6829	12.5995	9.0433	0.21

[a] $\delta_{\mathrm{RMS}}\ (\%) = 100\{(1/n)\sum[(u_{\mathrm{exptl}} - u_{\mathrm{calcd}})/u_{\mathrm{calcd}}]^2\}^{1/2}$; n is the number of points.

The ultrasonic speeds increase smoothly with pressure. The present results are represented by the following polynomial equation in pressure p,

$$u = \sum_{i=0}^{4} a_i p^i \qquad (1)$$

The coefficients a_i, calculated by the method of least squares, are listed in Table II with the percentage root-mean-square derviations δ_{RMS}. The results on speed in liquid dichlorotetrafluoroethane (R114), reported from our laboratory (*1*), are also plotted in Figure 1. In the case of this refrigerant, the values against pressure were fitted well to the polynomial formula of third order in pressure with the maximum deviation of 0.2% at temperatures from 283.15 to 323.15 K. The experimental values of speed in R13B1 show larger pressure dependence

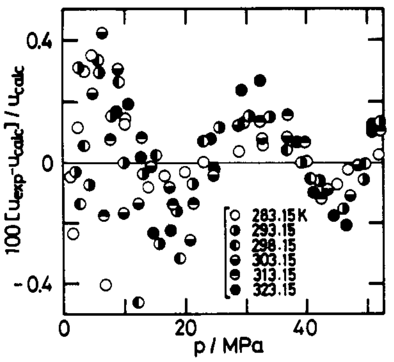

Figure 2. Deviation plot for ultrasonic speeds.

in the region of higher temperatures and lower pressures. Similar behavior has been observed for other thermodynamic properties, i.e., *pVT* (*7*) and isobaric specific heat capacity (*8*). To represent the data in this region, an equation of fourth order in pressure is necessary. But even then, eq 1 does not reproduce satisfactorily the experimental values near saturated vapor pressure as shown in Figure 2.

In these measurements, relatively large absorption of the acoustic wave in liquid R13B1 occurred in spite of careful liquefaction of the sample with no remaining vapor. This absorption gives rise to the distortion of electric signal observing period *t*, that is, the irregularity of experimental ultrasonic speed. According to studies on the absorption of sound in liquids (*9*, *10*), at low frequency the acoustic waves in substances including bromine atoms show a large difference of absorption in each liquid, and existence of bromine atoms is not confirmed in general to lead to the large absorption. The large absorption is known to occur in liquids which have symmetrical structure such as benzene rather than those which contain a bromine atom. The ultrasonic speed in benzene can be observed normally by use of an instrument in this work.

The critical temperatures of R114 (*11*) and R13B1 (*5*) are 418.85 and 340.15 K, respectively. So the temperatures used in this work are close to the critical temperature of the sample. In the critical region of vapor-liquid transition, the ultrasonic speeds and absorption of ultrasonic waves have been measured for a number of substances, i.e., carbon dioxide (*10*, *12*) and xenon (*13*). It is indicated in these papers that in this region the speeds decrease and absorptions increase rapidly up to its critical temperature, and at critical temperature these quantities have the minimum and the maximum values, respectively. This phenomenon was usually explained by a relaxation mechanism involving the rearrangement of molecular "clusters" which was postulated by Schneider et al. (*13*, *14*). Therefore it seems reasonable to conclude that the relatively large absorption of ultrasonic waves for R13B1 in this work may be due to the fact that the measurement was carried out in the region near its critical temperature. From these facts, the probable uncertainty on the present results of ultrasonic speed was greater than that in pure benzene (maximum 0.2%) reported in previous work (*1*), and was 0.45% in the range up to 10 MPa and 0.28% above 10 MPa.

The ultrasonic speeds u_{p_s} at saturated vapor pressure p_s were estimated by extrapolation from the experimental values. The values of p_s required in this calculation were derived from equation reported in ref (*5*). The results are also listed in Table I and Figure 1. It is estimated that these extrapolated values have errors of a maximum of 1.2% caused by the absorption of acoustic wave, as described above, and the meagerness of data in the vicinity of vapor pressure at higher temperature.

In this work, the ultrasonic speeds in the liquid phase of bromotrifluoromethane (R13B1) were measured at several temperatures and pressures. The results show at first extremely low values, and then increase rapidly with pressure. This behavior is different from those in refrigerant R114 obtained in our recent paper (*1*); for example, the values of speed u and its pressure dependence $(\partial u/\partial p)_T$ at 298.15 K and 10 MPa are 407.2 $m{\cdot}s^{-1}$, 9.42 $m{\cdot}s^{-1}{\cdot}MPa^{-1}$ for R13B1 and 622.6 $m{\cdot}s^{-1}$, 6.95 $m{\cdot}s^{-1}{\cdot}MPa^{-1}$ for R114, respectively. The variations of ultrasonic speed with temperature and pressure thus obtained may afford an important information for understanding the behavior of refrigerant fluids.

Registry No. $CBrF_3$, 75-63-8.

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