Ultrasonic Speeds in Liquid Phase of Dichlorotetrafluoroethane (R114) under High Pressures

Toshiharu Takagi* and Hiroshi Teranishi

Department of Chemistry, Faculty of Engineering and Design, Kyoto Institute of Technology, Matsugasaki, Sakyoku, Kyoto 606, Japan

The ultrasonic speeds in the liquid phase of dichlorotetrafluoroethane (R114) were measured over the ranges from 283.15 to 323.15 K and from near its saturated vapor pressure to about 50 MPa. In order to perform this measurement, an apparatus with sing-around technique employing a fixed-path ultrasonic interferometer operating at a frequency of 2 MHz was constructed. By comparisons to ultrasonic speeds in benzene which were measured and reported in the literature, the accuracy of the interferometer was confirmed to be better than ±1.8 m·s^{-1} for the experimental conditions reported here.

Introduction

The thermodynamic properties for fluorocarbon refrigerants in the gas and/or the liquid phase, such as pVT values (*1*, *2*) and isobaric heat capacity (*3*, *4*), have been investigated experimentally or theoretically for wide ranges of temperature and pressure. Since ultrasonic speed gives a powerful clue to the thermodynamic behavior of a fluid, a significant number of measurements of this property are being made for some organic liquids (*5–8*). The values of ultrasonic speed in the gas phase of refrigerants are derived in most cases from equations of state of various types (*9–11*). Kokernak and Feldman (*12*) measured the ultrasonic speed for states in the liquid phase of dichlorodifluoromethane (R12), and estimated the ultrasonic speed for other refrigerants using a theoretical rule. However, experimental data on the ultrasonic speed in refrigerants under high pressure are rarely reported. This work describes a precise instrument with sing-around technique employing fixed-path ultrasonic interferometer operated at a frequency of 2 MHz, and presents new experimental data of the ultrasonic speed in the liquid phase of dichlorotetrafluoroethane (R114) in the ranges of temperature from 283.15 to 323.15 K and pressures from near its saturated vapor pressure to about 50 MPa.

Experimental Section

Material. Dichlorotetrafluoroethane $CClF_2$–$CClF_2$ (R114) was supplied by Daikin Kogyo Co. It contained about 5% isomer CCl_2F–CF_3 (R114a), and the purity, including this isomer, was better than 99.9 wt %. This isomer resembles $CClF_2$–$CClF_2$ very closely in physicochemical properties. Therefore the separation of R114 and R114a in purification process and the quantitative analysis of the both components are extremely difficult. The mixtue was used without further purification, assuming that the 5% isomer would not significantly affect the thermodynamic properties.

Apparatus. The method used for measurement of ultrasonic speed was a sing-around technique (Cho-onpa Ind. Co., UVM-2) with fixed-path ultrasonic interferometer employing a gated amplifier. The interferometer is shown in Figure 1. The transducer and reflector were maintained in parallel by rings and springs made of SUS 304 stainless steel. A short acoustic pulse, which was excited by the transducer (lead zircontitanate, PZT, 20 mm in diameter, 2 MHz), traveled over the known distance L in the sample. When the wave, after being reflected

Table I. Comparison^a of the Observed Ultrasound Speed $u/(m \cdot s^{-1})$ in Benzene with Literature Values at 298.15 K

p/MPa	u_a	u_b	u_c
0.1	1300.9	1301.6	1301.1
10.0	1348.1	1348.2	1347.8
20.0	1393.0	1393.1	1392.8
30.0	1434.7	1434.7	1434.6
40.0	1474.6	1472.8	1475.4
50.0	1509.3	1508.7	1510.6

$^a u_a$, this work; u_b, ref *13*; u_c, ref *6*.

by the reflector, returned to the transducer, the gate was opened electrically by the gated amplifier, and the signal was detected by the same transducer. In this work a delay line was employed to avoid the interference of multiple echoes. The next acoustic short pulse was generated a definite time (delay time τ = 511.272 ± 0.0016 μs) after the arrival of the reflected wave. The ultrasonic speed u was obtained from the average value of one thousand periods t including the delay time τ, as given by the following equation

$$u = 2L/(t - \tau) \tag{1}$$

The distance L (=12.692 ± 0.003 mm) in the interferometer was obtained from the measured period in benzene in the ranges of temperatures from 283.15 to 323.15 K and at atmospheric pressure where the precise speed is known from previous literature (*6*, *13*). Figure 2 is a functional diagram of the whole setup. The interferometer was placed in a high-pressure vessel made of SUS 420 stainless steel, which was immersed in a water bath controlled within ±0.03 K from 293.15 to 323.15 K, and within ±0.05 K for 283.15 K. The temperature was observed by a thermocouple of T type calibrated by standard thermometer. The pressure applied to the sample was generated by means of a hand oil pump, and transmitted through mercury in the Hg cylinder. At each experimental condition, the pressure was measured by a precise Bourdon gauge (Nagano Keiki Ltd. 10A-2) of full scale 5 MPa and a strain gauge (Toyo Baldwin Co., Ltd. HT-200, TPS-2300) of full scale 200 MPa. These gauges were calibrated by a deadweight tester within ±0.015 MPa of scale up to 5 MPa and within ±0.13 MPa in the range from 5 to 50 MPa. The time interval of the electric signals and thermometer and strain gauge readings were recorded by a digital volt meter (DVM), and reduced by a microcomputer to get the respective experimental values. The sample fluid was charged after the sample chamber in the high-pressure vessel and the Hg cylinder (sample side) were evacuated with a vacuum pump, and the measurements were started at regular time intervals (about 25 min) after each experimental condition was stabilized.

Results and Discussion

Preliminary Runs. As a preliminary study, the ultrasonic speeds u in pure benzene (chromatographic grade) were measured at 298.15 K and up to 50 MPa, and the results are listed in Table I. Bobic (*6*) measured the u values in benzene at several temperatures and pressures up to the freezing pressures by using the pulse-echo technique. Our previous
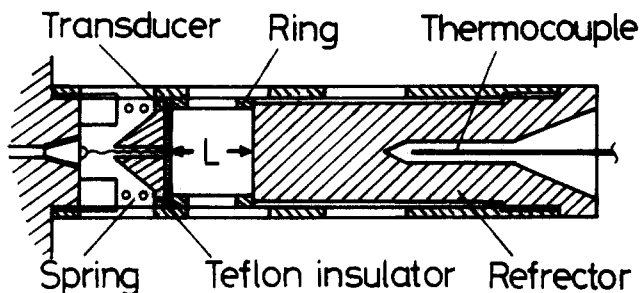
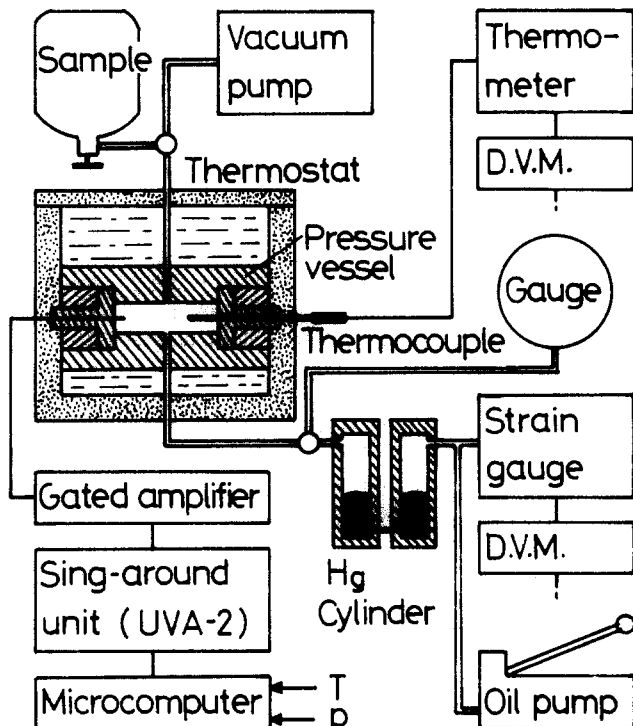**Figure 1.** Fixed-path ultrasonic interferometer (L = 12.692 ± 0.003 mm).

Figure 2. Block diagram of ultrasonic speed apparatus.

Table II. Ultrasonic Speeds $u/(\text{m} \cdot \text{s}^{-1})$ in Liquid Phase of Dichlorodifluoroethane (R114) at Several Pressures p/MPa

p	u	p	u	p	u	p	u
283.15 K		21.34	706.6	303.15 K		13.31	604.8
0.128[a]	601.6[b]	25.31	727.0	0.251[a]	536.8[b]	17.34	630.7
0.38	603.5	29.73	748.1	0.35	536.8	20.76	650.8
0.69	606.1	34.13	768.1	0.78	540.9	24.38	671.0
1.05	607.8	38.47	787.9	1.24	544.9	28.48	692.6
1.78	613.1	43.89	809.0	2.46	555.6	31.87	709.4
2.27	616.4	49.46	830.7	4.09	568.3	35.80	727.9
2.58	620.0			5.80	581.2	39.58	744.9
3.61	627.2	298.15 K		7.78	595.7	43.56	762.7
6.45	646.9	0.214[a]	550.8[b]	10.39	614.0	46.58	775.1
10.23	670.5	0.67	554.0	12.85	630.0	50.60	791.3
15.52	701.3	1.16	557.9	15.50	646.5		
19.80	722.8	1.58	561.4	18.69	665.0	323.15 K	
24.62	745.9	2.07	565.4	22.57	686.5	0.447[a]	467.3[b]
30.38	772.1	2.44	568.2	26.10	704.9	0.87	470.4
34.80	791.5	3.05	573.1	30.22	720.8	1.45	476.7
37.94	804.5	3.66	578.1	33.11	734.9	3.01	492.6
43.20	825.8	4.43	583.5	35.68	750.7	6.86	526.8
49.85	851.5	8.02	609.0	38.83	764.5	8.04	536.6
50.20	853.2	12.11	635.9	42.53	780.5	10.28	554.6
		15.79	658.2	45.59	792.9	13.81	580.2
293.15 K		20.28	683.4	49.84	809.8	17.08	602.0
0.181[a]	571.8[b]	24.23	704.2			19.85	619.5
0.28	572.2	29.01	728.0	313.15 K		23.47	640.9
0.33	572.8	34.11	751.7	0.338[a]	501.9[b]	27.22	661.7
0.71	575.6	39.40	774.7	0.36	501.4	30.23	677.7
1.75	584.1	43.69	792.8	0.41	501.9	33.07	691.9
3.25	595.5	47.73	808.9	0.55	503.5	36.39	706.2
6.62	619.1	50.66	820.1	1.29	510.8	39.32	721.6
9.59	638.8			2.58	522.8	42.35	735.4
13.03	660.3			4.84	541.9	45.33	748.2
16.94	682.9			7.64	564.2	49.65	766.3
				10.06	582.5	51.17	772.4

$^{a}p_{s}$. $^{b}u_{p_{s}}$.

Table III. Coefficients a_i for Eq 2 and Standard Deviation $\delta_{std}{}^{a}$

T/K	a_0	a_1	$-10^2 a_2$	$10^4 a_3$	δ_{std}, %
283.15	601.21	7.5759	8.2401	6.3118	0.078
293.15	571.59	7.6921	7.1412	4.4675	0.060
298.15	549.91	8.0160	7.8957	5.1965	0.049
303.15	535.89	8.3898	8.7668	6.0124	0.057
313.15	500.30	9.1542	10.4551	7.4598	0.083
323.15	463.85	10.0138	12.4991	9.3760	0.108

$^{a}\delta_{std}(\%) = 100\{1/n\sum[(u_{exptl} - u_{calcd})/u_{calcd}]^2\}^{1/2}$, where n = number of points.
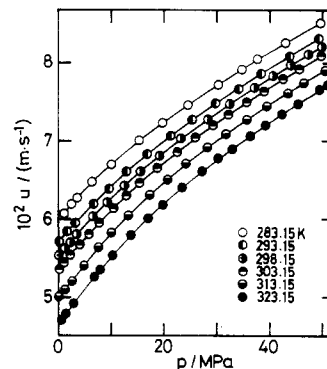
Figure 3. Pressure dependence of ultrasonic speed u in the liquid phase of refrigerant R114.

work (*13*) also reported the u values in benzene at various conditions of temperature and pressure measured by a sing-around technique with a variable-path ultrasonic interferometer. Therefore, the experimental values of these studies are listed in Table I in order to check the reliability of the present values. As can be seen clearly in this table, the values observed with the fixed-path interferometer in the present work agree with the values reported in ref *6* and *13* within ±1.3 m·s⁻¹ in the present pressure range. Moreover, at each experimental condition, the values of u were reproduced within an accuracy of ±1.0 m·s⁻¹ in repeated runs. Consequently, the probable accuracy in the measurements of speed by a new apparatus is estimated, taking into account the observed errors and the influence on distance L caused by temperature or pressure change, to be less than ±1.8 m·s⁻¹ over the whole range of the experiment.

Ultrasonic Speed in Refrigerant. The ultrasonic speed u in the liquid phase of dichlorotetrafluoroethane (R114) at various temperatures T and pressures P observed by the new instrument are listed in Table II. The u values at each temperature increase smoothly with increasing pressure over the whole range used in the present experiment, as shown in Figure 3. For each temperature the variations in speed u with pressure p were used to determine, by the method of least squares, values of coefficients in a smoothing equation as follows

$$u/(\text{m} \cdot \text{s}^{-1}) = \sum_{i=0}^{3} a_i(p/\text{MPa})^i \qquad (2)$$

Values of the coefficients a_i are listed in Table III together with the standard deviations δ_{std}. The experimental u values in the present fluid agree with the estimated u values from eq 2 with deviations not exceeding ±0.2% throughout the temperature and pressure range of the experiments as illustrated graphically in Figure 4. However, the figure shows irregularities in the deviations in the lower pressure region. This suggests that the
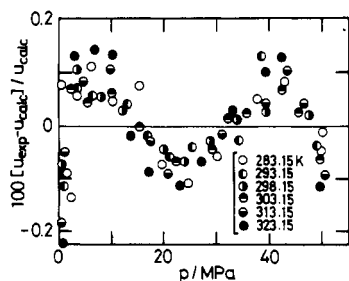
Figure 4. Deviation plot for ultrasonic speed u.

ultrasonic speeds are strongly dependent upon pressure close to the saturated vapor pressure especially at high temperature. This tendency is similar to that of other thermodynamic properties, i.e., the pVT relation (2) and isobaric heat capacity (4).

From the coefficients for eq 2, the speed in the liquid phase u_{p_s} at the vapor pressure p_s was calculated, and the results are also shown in Table II with the p_s derived from the equation reported in ref 14. Saklades and Costes (15) estimated the additivity coefficient B from molecular structural considerations using the experimental u values, and calculated the value of speed u by Rao's equation (16) $[u = (Bp/M)^3$, where p = density, M = molecular weight]. It is well-known that this method can be adapted conveniently to some organic liquids at atmospheric pressure. Kokernak and Feldman (12) measured the ultrasonic speed in the liquid phase of dichlorodifluoromethane (R12), and calculated the B value for the fluorine atom. From this value and the B values of other atoms estimated by Saklades and Costes, the speeds in some liquids including fluorinated hydrocarbons were estimated. According to their report, the u value in the liquid phase of dichlorotetrafluoroethane (R114) at 298.15 K was 478.5 m·s^{-1}. However,

this value is lower by about 15% than that obtained by eq 2 in this work. The vapor pressures are 0.6516 MPa for R12 (17) and 0.2144 MPa for R114 (14) at 298.15 K. In ref 12, the ultrasonic speed in R114 was obtained by using the additivity coefficients of fluorine atom taken from the u value in R12, which has a different vapor pressure from that for R114. Thus, a large discrepancy in ultrasonic speed would be expected between these two refrigerants. It may be presumed that application of this theoretical method to predict the ultrasonic speed in refrigerants is unreasonable. Consequently, direct measurements of ultrasonic speed in the liquid phase of individual refrigerants are expected to continue in the future.

Literature Cited

(1) Martin, J. J. *J. Chem. Eng. Data* **1980**, *5*, 334.
(2) Wilson, D. P.; Hules, K. R. *Proc. 8th Symp. Thermophys. Prop., New York* **1981**, Vol. II, 361.
(3) Kudchadker, S. A.; Kudchadker, A. P. *J. Phys. Chem. Ref. Data* **1978**, *7*, 1285.
(4) Kolesov, V. P.; Kosarukina, E. A.; Zhogin, D. Yu.; Poloznikova, M. E.; Pentin, Yu. A. *J. Chem. Thermodyn.* **1981**, *13*, 115.
(5) Gammon, B. E. *J. Chem. Phys.* **1978**, *64*, 2556.
(6) Bobic, M. *J. Chem. Thermodyn.* **1978**, *10*, 1137.
(7) Takagi, T.; Teranishi, H. *J. Chem. Thermodyn.* **1982**, *14*, 577.
(8) Takagi, T.; Teranishi, H. *J. Chem. Thermodyn.* **1984**, *16*, 1031.
(9) Downing, R. C.; Long, Jr. L. *ASHRAE J.* **1983**, *5*(3), 41.
(10) Perilshtein, I. I.; Kuslyalkin, G. A. *Kholod. Tekh.* **1978**, 38.
(11) Doring, R. *Int. Congr. Refrig.* **1978**, *2*, 77.
(12) Kokemak, R. P.; Feldman, C. L. *ASHRAE J.* **1971**, *13*(7), 59.
(13) Takagi, T.; Teranishi, H. *J. Soc. Mater. Sci., Jpn.* **1984**, *33*, 134.
(14) Hasegawa, N.; Wada, S.; Uematsu, M.; Watanabe, K. *Proc. 16th Int. Congr. Refrig., Paris* **1984**, Vol. II, 31.
(15) Saklades, B. C.; Costes, J. *AIChE J.* **1955**, *1*, 274.
(16) Rao, R. *J. Chem. Phys.* **1941**, *9*, 682.
(17) Michels, A.; Wassenaar, T.; Wolkers, G. L.; Prins, CHR.; Klundert, L. v. d. *J. Chem. Eng. Data* **1966**, *11*, 449.

Viscosities, Densities, and Activation Energies of Viscous Flow of the Ternary Systems *n*-Hexane–Benzyl Alcohol–Toluene, *n*-Hexane–Benzyl Alcohol–Chlorobenzene, and *n*-Hexane–Benzyl Alcohol–1-Hexanol and Their Partially Miscible Binary Subsystem *n*-Hexane–Benzyl Alcohol at 30, 40, 50, and 60 °C

Ramesh P. Singh,* Chandreshwar P. Sinha,† and Basuki N. Singh‡

Department of Chemistry, Bhagalpur College of Engineering, Bhagalpur-813210, India

Mixture viscosities and densities of the partially miscible ternary systems of toluene, chlorobenzene, and 1-hexanol with their partially miscible binary subsystem *n*-hexane–benzyl alcohol were measured at 30, 40, 50, and 60 °C. Activation enthalpies and entropies for viscous flow have been obtained and their variations with composition have been discussed.

Introduction

Viscosities and activation energies of viscous flow of several binary as well as ternary mixtures, reported by us earlier (1–5), dealt with systems which are completely miscible in the temperature range studied. Herein are results of our similar investigation of the partially miscible ternary systems *n*-hexane (1)–benzyl alcohol (2)–toluene (3), *n*-hexane, (1)–benzyl alcohol (2)–chlorobenzene (3), and *n*-hexane (1)–benzyl alcohol (2)–1-hexanol (3) and their partially miscible binary subsystem *n*-hexane (1)–benzyl alcohol (2) at 30, 40, 50, and 60 °C.

Experimental Section

Materials. Liquids used were the same as in the previous studies (1–5). However, their purity, after fractional distillation

†Present address: Department of Chemistry, Ananda Chandra College, Jalpaiguri-735101, W. Bengal, India.
‡Present address: Department of Chemistry, Mahendra Morang Campus, Biratnagar, Nepal.