Speed of Sound in Saturated Liquid Trichlorofluoromethane

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The speed of sound in saturated liquid trichlorofluoromethane has been measured in the temperature range −25 to 77 °C at 7 MHz. These data were combined with available density data to obtain the adiabatic compressibilities. These new measurements of the speed of sound are different from those reported for cryogenic fluids, but they are similar to those of tetrachloromethane.

Introduction

There is current and increasing interest in the halogenated hydrocarbons due to their molecular characteristics and industrial applications. The data presented here were obtained as a part of an experimental program to investigate thermodynamic properties of some pure fluids. Measurements of the speed of sound in saturated liquid trichlorofluoromethane (Freon 11, CCl_3F) have been made at the frequency of 7 MHz from −25 to 77 °C.

The relation between the speed of sound, density ρ, and isentropic compressibility β_s was used with the available density data to obtain β_s from the measured speed of sound.

Experimental Procedure

The method used to measure the speed of sound was the pulse-echo technique developed by Greenspan and Tschiegg (*1*). The apparatus was similar to the one described in detail by Younglove (*2*). Only a brief summary will be given here. Two plane parallel X-cut quartz crystals (1.27 cm in diameter) are pressed to the ends of a tubular stainless-steel spacer (1 cm in length) by two electrode springs. One crystal, the emitter, is excited by an electrical pulse of ~4 V and 0.13-μs duration. This pulse makes the crystal vibrate at its fundamental resonance frequency of 7 MHz, resulting in 10–20 oscillations which propagate through the fluid. This pressure wave is reflected back and forth between the crystals. An output signal is obtained from the second crystal and is observed on an oscilloscope. The received signal is generated by the pressure wave in the sample striking the receiving crystal. Successive acoustic signals result from echoes which have made multiple transits through the space length. The electrical pulse repetition rate can be adjusted so that the arrival time of a pulse echo at the receiving crystal coincides with that of the succeeding directly received pulse. This is observed on the oscilloscope as a single pulse of higher amplitude. Under these conditions, the speed of sound W is determined by

$$W = 2df$$

where d is the length of the spacer and f is the pulse repetition frequency. The sharpness of the observed superposition of the pulse echo and the accuracy in the measurement of d give the uncertainty in W. A frequency counter with a resolution of 0.1 Hz and an accuracy of 1 Hz was used to measure f. However, Δf was estimated as ±5 Hz from the experimentally observed pulse-echo superposition. The length of the spacer was measured at 20 °C at eight different points along the circumference with a deviation Δd less than 1 μm. Such distance was corrected for temperature expansion within the same precision.

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Table I. Speeds of Sound W_{exptl} and Derived Values of the Isentropic Compressibility β_s in Saturated Liquid Trichlorofluoromethane[a]

t/°C	W_{exptl}/(m s^{-1})	$100\Delta W/W$	ρ_o/(kg m^{-3})	β_s/(GPa)$^{-1}$
−24.91	916.1	0.028	1589.6	0.7499
−19.92	898.1	0.000	1578.7	0.7853
−14.97	880.4	−0.004	1567.9	0.8227
−10.02	862.9	0.002	1556.8	0.8627
−5.06	845.2	−0.024	1545.7	0.9052
−0.12	828.0	−0.005	1534.5	0.9503
4.81	810.8	−0.002	1523.2	0.9987
9.86	793.2	−0.003	1511.5	1.0513
14.93	775.5	−0.023	1499.6	1.1082
19.97	758.2	−0.015	1487.7	1.1690
25.00	741.0	0.001	1475.7	1.2341
29.76	724.5	−0.024	1464.2	1.3004
35.04	706.8	0.006	1451.4	1.3796
40.08	689.8	0.021	1439.0	1.4613
45.11	672.8	0.019	1426.6	1.5495
50.02	656.2	0.005	1414.3	1.6426
54.70	640.7	0.041	1402.5	1.7381
55.82	636.9	0.023	1399.7	1.7624
57.89	629.9	0.014	1394.4	1.8081
59.64	623.9	−0.012	1389.9	1.8477
61.68	617.2	0.002	1384.2	1.8966
63.71	610.5	0.004	1378.9	1.9458
65.79	603.6	−0.009	1373.4	1.9985
67.82	597.0	0.011	1368.0	2.0516
69.42	591.6	−0.003	1363.8	2.0951
71.44	585.0	−0.003	1358.3	2.1512
73.29	579.2	0.052	1353.3	2.2050
75.40	571.7	−0.048	1347.5	2.2682
77.43	565.0	−0.056	1341.9	2.3320

[a] Column 3 gives the percent deviation $(W_{exptl} - W_{calcd})100/W_{calcd}$. W_{calcd} from eq 1.

The length of $d = 9887 \pm 1$ μm was chosen to minimize signal losses by absorption. Below 20 °C the pressure was measured with a bourdon gauge to ensure that the measurements were made along the saturation line. However we were unable to measure it above room temperature because of condensation of the fluid inside the pressure gauge. Therefore, at each temperature, the sound speed was measured at least twice with some Freon 11 being removed from the sample holder between measurements. Identical sound-speed observations indicated that the two-phase condition existed in the sample holder. The uncertainty in the speed of sound measured with the pulse-echo technique is estimated to be less than 0.05%. The temperatures were measured with a platinum resistor calibrated on the IPTS-68. The maximum uncertainty in the measured temperature was estimated to be less than 0.05 °C. The fluid sample was obtained by successively degassing and freezing commercially available industrial trichlorofluoromethane. A minimum purity of 99.6% was obtained according to chromatographic analysis.

Results and Discussion

Measurements of the speed of sound in saturated liquid Freon 11 have been made at ~5 °C intervals (or less) from −25 to 77 °C. These data were fitted to an quadratic equation of the form

$$W(t) = a + bt + ct^2$$

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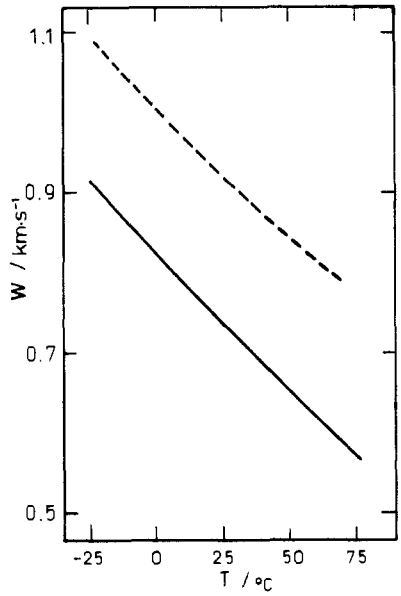

Figure 1. Speed of sound in saturated liquid CCl_3F (—) and CCl_4 (---) as a function of temperature.

where a, b, and c were found by an unweighted least-squares method. The coefficients and their standard deviations obtained are as follows: $a = 827.66$, $\sigma_a = 0.29$; $b = -3.0541$, $\sigma_b = 0.0145$; $c = 0.00150$, $\sigma_c = 0.00023$. The number of digits of these coefficients is given to reproduce Table I, and not all are necessarily significant. Deviations of the data from eq 1 appear to be random and less than the estimated experimental uncertainty of 0.05%. The measured values of the speed of sound are tabulated together with percent differences in Table I. Five measurements around a selected temperature on different days indicated reproducibilities better than 0.03%.

The only published data of the speed of sound in Freon 11 are those of Redkozubov (*3*) but were unavailable for comparison at the time of writing this report. Qualitatively, the data as a function of temperature show a positive curvature in contrast with those of other cryogenic fluids that have a negative curvature in their full vapor-pressure temperature ranges (*4*). However, the speed of sound data for CCl_4 published by Rowlinson (*5*) also show a positive curvature. These CCl_4 data were fitted to a quadratic expression as eq 1 and are shown together with those of CCl_3F in Figure 1.

The measured speed of sound data have been combined with the orthobaric densities represented by the equations of Benning and McHarness (*6*) to calculate adiabatic compressibilities. The latter are also shown in Table I.

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Vapor Pressures of Bromine–Quaternary Ammonium Salt Complexes for Zinc–Bromine Battery Applications

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Vapor pressures were measured for three bromine complexes: (1) tetramethylammonium bromide–bromine, (2) *N*-ethyl-*N*-methylmorpholinium bromide–bromine, and (3) trioctylmethylammonium chloride–bromine complexes. From the Clausius–Clapeyron equation, vapor pressure–temperature data obtained in the temperature range 0–40 °C were correlated to provide a least-squares curve fit. Calculated molar heats of vaporization for the three complexes listed in the preceding order are 10.0, 11.7, and 16.8 kcal/mol of bromine, respectively.

Introduction

Several bromine complexes are being explored as carriers of the electrochemically acitve bromine component for use in zinc bromine batteries (*1*). Vapor-pressure data for these complexes are useful in describing the operational characteristics of the battery and in estimating the release of bromine vapor in the event of an accidental spill of the complex. The gas-phase concentration of bromine vapor over the complex surface is dictated by the vapor pressure exerted by the complex at a given temperature. Vapor pressures of three complexes, tetramethylammonium bromide–bromine (TMAB–Br), *N*-ethyl-*N*-methylmorpholinium bromide–bromine (NENMMB–Br), and trioctylmethylammonium chloride–bromine (TOMAC–Br) were measured and fitted to the integrated Clausius–Clapeyron equation. The molar heat of vaporization for each of the three complexes was also calculated.

Experimental Procedure

Preparation of Bromine Complexes. The bromine complexes selected for this study are not produced commercially and were synthesized in our laboratory. The synthesis of the complexes was accomplished by the following procedures.

(1) TMAB–Br Complex: Tertramethylammonium bromide (3 mol) was dissolved in 500 mL of distilled water to obtain a saturated solution. Bromine (6 mol) was added slowly to the saturated solution of tetramethylamminoum bromide, and the mixture stirred vigorously. The stirred solution was kept still for several days in a desiccator until a yellow aqueous layer separated from a dark red liquid which was the desired TMAB–Br

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