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High Pressure Measurements of Density, Velocity of Sound, and Bulk Moduli of Pentane and 2-Methylbutane and Their Mixtures

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Dilatometric and ultrasonic measurements were made on mixtures of pentane and 2-methylbutane to give density, relative volume, isothermal bulk modulus, velocity of sound, and adiabatic bulk modulus to pressure of 24 kilobars (2.4×10^9 N/m^2).

Key words: Bulk modulus; compressibility; density; dilatometric measurements; high pressure; liquids; 2-methylbutane; pentane; ultrasonics.

1. Introduction

This report supplements a previous report [1][1] which gave the results of measurements of mixtures of 2-methylbutane and aviation instrument oil to 20 kilobars.[2] Mixtures of pentane and 2-methylbutane are used as hydrostatic pressure fluids to 50 kilobars [2]. These pressures are well above the freezing pressures of the individual fluids. A study was undertaken to determine the properties of the mixtures as a function of pressure at room temperature. The freezing pressure at room temperature, given by Reeves et al [4], is 15 kbar for pentane and is 21 kbar for 2-methylbutane. The freezing pressure of pentane was measured to be 17.55 ± 0.67 kbar by Gelles [5]. Our experiments show the pressure required at 22 °C for initiation of freezing to be 25 kbar for pentane and 29 kbar for 2-methylbutane with equilibrium freezing pressures of 18.2 ± 0.5 kbar and 22.5 ± 0.5 kbar respectively.

The equilibrium freezing pressures were determined by over-pressurizing the fluid sufficiently to initiate freezing, then reducing the pressure to partially melt the solid, and then increasing the pressure to partially refreeze the liquid in contact with the solid. The average of the melting pressure and this refreezing pressure is taken as equilibrium freezing pressure. Attempts to determine freezing pressures of various mixtures of the pentanes were unsuccessful. One mixture of 90 percent pentane–10 percent 2-methylbutane appeared to freeze at 27 kbar but five other attempts to freeze similar mixtures were unsuccessful at pressures of 30 to 39 kbar. One mixture of 75 percent pentane–25 percent 2-methylbutane appeared to freeze at 33 kbar but a second mixture failed to freeze at 39 kbar. Other mixtures showed no freezing at 39 to 44 kbar. While no satisfactory freezing determinations were made for the mixtures the properties determined for the mixtures as well as the pure substances to 24 kbar are presented. The pure pentanes are in the supercooled (superpressurized) state above their equilibrium freezing pressures.

2. Low-Pressure Measurements (Atmospheric Pressure)

The densities of the mixtures were determined by weighing known volumes of the fluids. The same 10 MHz transducer and electronic equipment which are used for the high pressure ultrasonic measurements, described in reference [3], were arranged with a separate vessel to measure the velocity of sound of the mixtures at atmospheric pressure. The adiabatic bulk modulus, B_s, is calculated from $B_s = \rho c^2$ where ρ is the density and c is the velocity of sound. The low pressure dilatomer [1] was used to measure the isothermal bulk modulus of the mixtures. Smoothed values of these results as well as the ratio of the adiabatic to isothermal bulk moduli are given in table 1 for a temperature 22 °C.

[1] Figures in brackets indicate the literature references at the end of this paper.
[2] 1 kilobar = 10^8 N/m^2.

TABLE 1. *Density, Velocity of Sound, Isothermal and Adiabatic Bulk Moduli, and the Ratio of the Bulk Moduli at Atmospheric Pressure of Mixtures of Pentane and 2-Methylbutane.*

Ratio of pentane to 2-methylbutane	ρ kg/m^3	c m/s	B_T^* kbar	B_s kbar	B_s/B_T^*
0 – 100	618.	980	4.5	5.93	1.32
10 – 90	618.	983	4.5	5.97	1.33
25 – 75	619.	990	4.6	6.07	1.32
50 – 50	621.	1000	4.9	6.21	1.27
75 – 25	622.	1012	5.1	6.37	1.25
90 – 10	624.	1016	5.1	6.44	1.26
100 – 0	624.	1020	5.1	6.49	1.27

The density measurements for pentane (624 kg/m^3) and for 2-methylbutane (618 kg/m^3) agree with the values 624 and 620 respectively taken from Bridgman [6] and the values 624 and 618 respectively taken from Timmerman [7].

The velocity of sound measurement for pentane (1020 m/s) is in fair agreement with the values, corrected by means of reported temperature dependence to 22 °C, of 999 m/s taken from Schaaffs [8], 1015 m/s taken from Swanson [9], and 1035 m/s taken from Schaaffs [10].

The velocity of sound in 2-methylbutane (980 m/s) differs from the value 1007 m/s taken from Schaaffs [10] by approximately the amount of the spread of the values for pentane.

The values of isothermal bulk modulus ($B_T^* = -V dp/dV$) for pentane (5.1 kbar) and 2-methylbutane (4.5 kbar) are greater than the values of 3.0 kbar and 3.1 kbar respectively which were extrapolated from values calculated from Bridgman [6]. The isothermal bulk modulus for 2-methylbutane calculated from data in the International Critical Tables (I.C.T.) [11] is 4.3 kbar.

The ratio of adiabatic to isothermal bulk modulus of 1.27 for pentane agrees with 1.20 taken from Bergman [12] and the ratio of 1.32 for 2-methylbutane agrees with 1.32 taken from I.C.T. [11].

3. High-Pressure Measurements

A piston and supported cylinder device which uses a polyethylene (PETH) sleeve to contain the fluid is described in [1] and [3]. The position of the piston is followed by dial gages and appropriate corrections are applied for friction, piston compression, cylinder expansion, and the compression of the polyethylene sleeve. The length of the sample volume and the relative volume of the fluid to the volume at atmospheric pressure is determined. A quartz transducer is bonded to the closure plate in order that an ultrasonic pulse can be sent through the plate. The time difference between the arrival of a partial reflection of the pulse at the first passage from the closure plate to the sample and the arrival after passage through the sample and back is determined by an oscilloscope with a calibrated delay. This time of flight and the length of the sample permit the determination of the velocity of sound in the fluid at pressure. Such measurements were made to maximum pressures of 26 to 44 kbar with various mixtures of the pentanes to measure relative volumes and velocities of sound. These parameters, combined with the low-pressure determinations, were used to determine the bulk moduli and the ratios of the bulk moduli. The values from atmospheric pressure determinations are used for the 0 kbar points in all the tables and figures.

4. Results

Figure 1 shows the relative volume, the ratio of the volume at pressure to the volume at atmospheric pressure (V/V_0), of individual samples of pentane and of 2-methylbutane. The volume change at 25 and 29 kbar respectively show the freezing at overpressurization. Figure 2 shows the relative volumes at

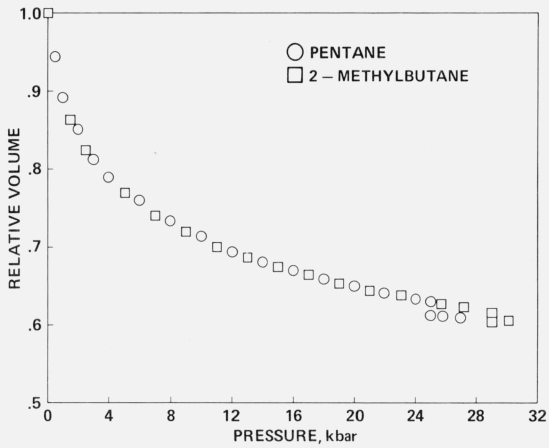

FIGURE 1. *Relative volumes of pentane and 2-methylbutane showing freezing.*

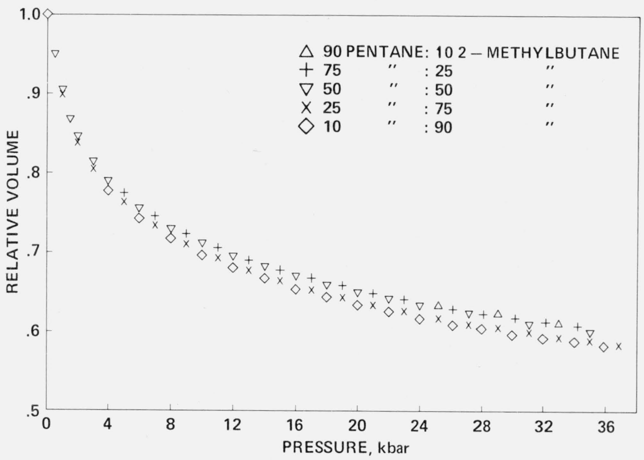

FIGURE 2. *Relative volumes of mixtures of pentane and 2-methylbutane to 24 kbar.*

TABLE 2. *Ratio of* V/V_0

Pressure in kilobars	Ratio of pentane to 2-methylbutane						
	100–0	90–10	75–25	50–50	25–75	10–90	0–100
0	1.000	1.000	1.000	1.000	1.000	1.000	1.000
2	.848	.847	.847	.846	.838	.838	.841
4	.794	.790	.790	.790	.780	.779	.787
6	.761	.756	.756	.756	.747	.746	.754
8	.738	.731	.731	.732	.722	.721	.730
10	.719	.712	.711	.713	.702	.701	.711
12	.702	.695	.696	.697	.686	.685	.696
14	.689	.682	.681	.683	.672	.672	.683
16	.678	.669	.670	.672	.660	.660	.671
18	.667	.659	.659	.661	.649	.649	.661
20	.658	.649	.649	.651	.640	.640	.652
22	.650	.641	.639	.643	.631	.631	.643
24	.643	.633	.633	.635	.623	.624	.636

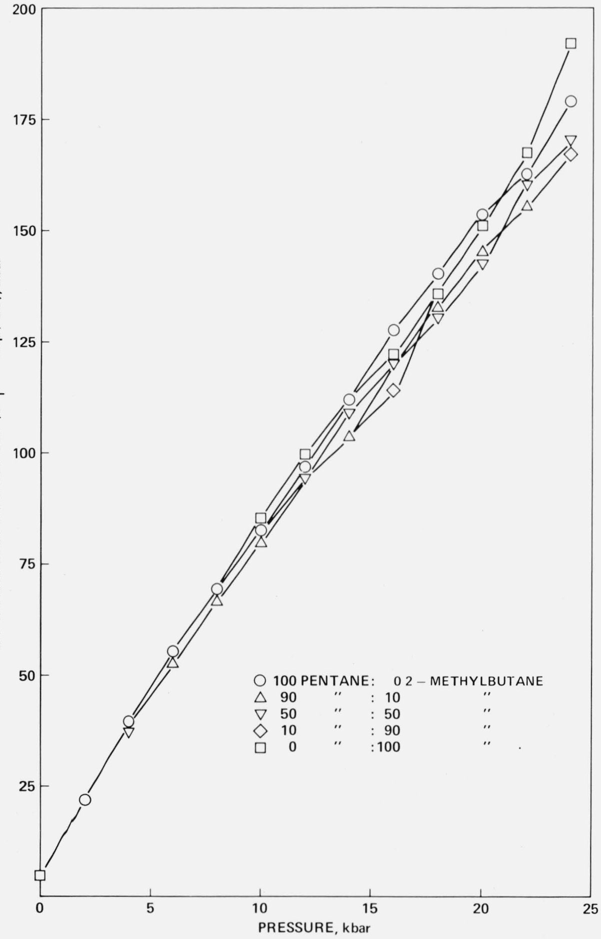

FIGURE 3. *Isothermal bulk modulus* ($B_T^* = -V\,dp/dV$) *of mixtures of pentane and 2-methylbutane to 24 kbar.*

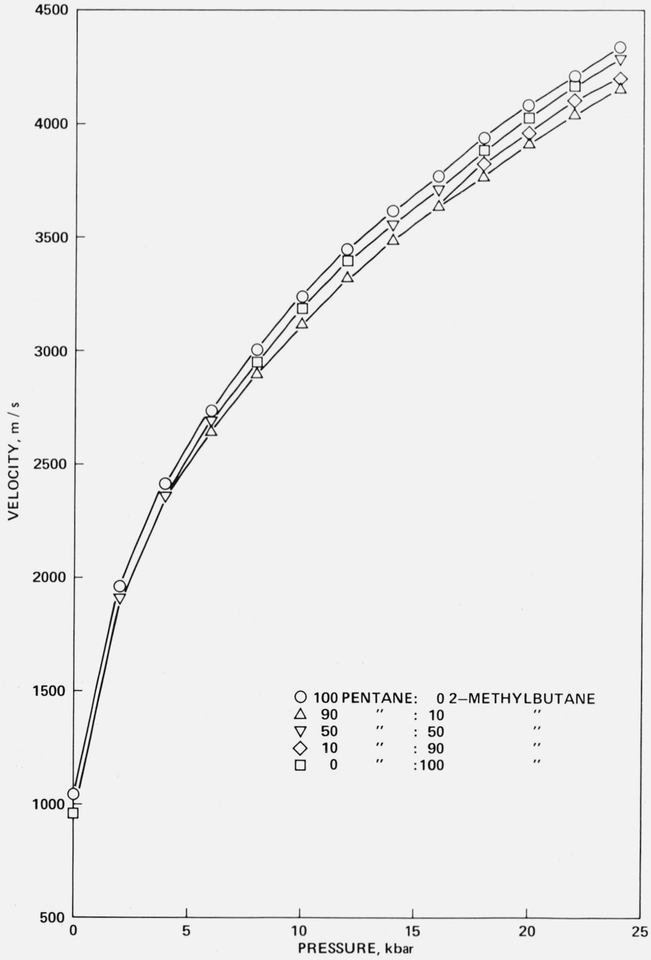

FIGURE 4. *Velocity of sound of mixtures of pentane and 2-methylbutane to 24 kbar.*

552-907 OL - 74 - 5

pressure of individual runs on mixtures of pentane and 2-methylbutane. Table 2 shows the relative volumes at selected pressures of pentane and 2-methylbutane and their mixtures. Tables 2 through 6 and figures 3 through 6 contain results averaged from five

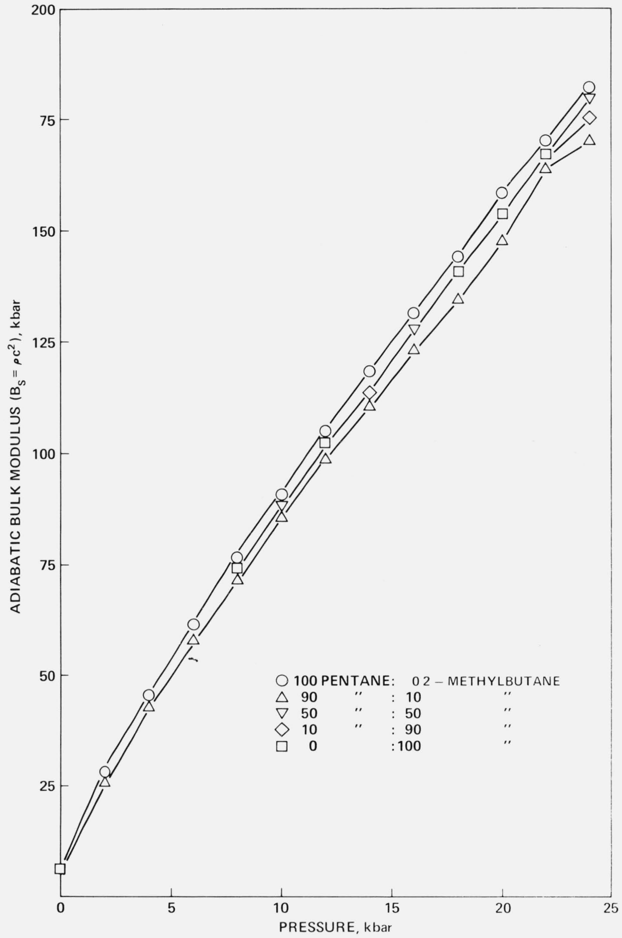

FIGURE 5. *Adiabatic bulk modulus* ($B_s=\rho c^2$) *of mixtures of pentane and 2-methylbutane to 24 kbar.*

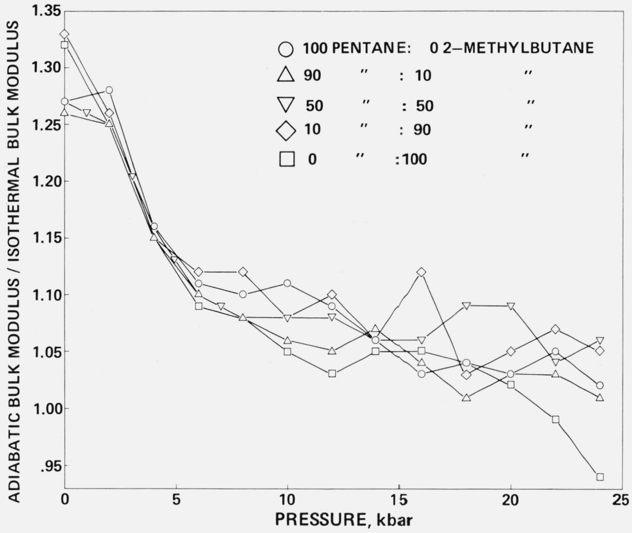

FIGURE 6. *Ratio of adiabatic to isothermal bulk moduli* ($B_s/B_T^*=c_p/c_v=1+T\alpha^2c^2/c_p$) *of mixtures of pentane and 2-methylbutane to 24 kbar.*

runs each for pentane, 2-methylbutane, and the 90 pentane to 10 2-methylbutane mixture; the results given for other mixtures are from single experiments. Table 3 and figure 3 show the isothermal bulk modulus ($B_T^*=-V dp/dV$). Table 4 and figure 4 show the velocity of sound in meters per second. Table 5 and figure 5 show the adiabatic bulk modulus ($B_s=\rho c^2$). Table 6 and figure 6 show the ratio of the adiabatic bulk modulus to the isothermal bulk modulus,

$$B_s/B_T^*=c_p/c_v=1+T\alpha^2c^2/c_p,$$

where α is the thermal expansivity, c_p the specific heat at constant pressure, and c_v the specific heat at constant volume. The total spread at 24 kbar for the five pentane runs is 2.4 percent in relative volume, 5.5 percent in velocity, 11 percent in isothermal bulk modulus, and 10.5 percent in adiabatic bulk modulus; for the five 2-methylbutane runs it is 1.1, 2, 9 and 5

TABLE 3. *Isothermal Bulk Modulus* (−Vdp/dV) *in Kilobars*

Pressure in kilobars	Ratio of pentane to 2-methylbutane						
	100–0	90–10	75–25	50–50	25–75	10–90	0–100
0	5.1	5.1	5.1	4.7	4.6	4.5	4.5
2	22.3	21.3	21.5	21.3	21.1	20.4	21.9
4	39.6	37.5	37.4	37.7	36.9	37.0	38.8
6	55.6	52.8	52.9	54.1	51.8	52.2	55.0
8	69.4	66.8	66.6	68.6	64.6	65.2	68.8
10	82.4	80.4	81.8	81.9	79.4	81.8	85.0
12	97.1	93.7	92.5	94.9	91.9	91.8	99.5
14	112.0	103.8	106.6	109.0	104.6	107.8	111.6
16	127.7	118.6	119.4	120.5	114.6	114.8	122.1
18	140.3	133.1	130.5	130.3	131.8	135.3	136.2
20	153.6	144.1	139.0	142.5	142.1	144.6	151.6
22	162.7	155.5	153.7	160.5	149.7	155.4	168.9
24	179.4	168.7	169.7	170.7	162.5	167.3	192.3

TABLE 4. *Velocity of Sound in Meters per Second*

Pressure in kilobars	Ratio of pentane to 2-methylbutane						
	100–0	90–10	75–25	50–50	25–75	10–90	0–100
0	1020	1016	1012	1000	990	983	980
2	1963	1900	1909	1903	1884	1860	1929
4	2416	2336	2343	2355	2323	2315	2383
6	2741	2650	2670	2698	2644	2650	2710
8	3004	2902	2918	2955	2901	2915	2971
10	3238	3123	3148	3181	3138	3147	3209
12	3444	3319	3336	3391	3333	3343	3401
14	3623	3488	3515	3560	3521	3525	3602
16	3782	3633	3659	3713	3704	3705	3742
18	3935	3773	3800	3891	3829	3834	3890
20	4091	3921	3954	4033	3939	3971	4033
22	4215	4048	4089	4161	4072	4113	4177
24	4336	4161	4226	4297	4226	4214	4316

TABLE 5. *Adiabatic Bulk Modulus in Kilobars*

Pressure in kilobars	Ratio of pentane to 2-methylbutane						
	100–0	90–10	75–25	50–50	25–75	10–90	0–100
0	6.5	6.4	6.4	6.2	6.1	6.0	5.9
2	28.4	26.6	26.8	26.6	26.3	25.6	27.4
4	45.9	43.1	43.3	43.7	42.9	42.6	44.6
6	61.6	58.0	58.8	59.8	58.0	58.3	60.1
8	76.3	71.8	72.6	74.0	72.3	73.0	74.5
10	91.1	85.5	86.6	88.1	86.9	87.4	89.3
12	105.3	98.8	99.6	102.4	100.4	100.9	102.4
14	118.8	111.3	112.8	117.9	114.3	114.5	117.1
16	131.6	122.9	124.4	127.4	128.8	128.6	128.5
18	144.6	134.7	136.4	142.1	139.9	140.0	141.1
20	158.4	147.6	149.8	154.9	150.2	152.4	153.8
22	170.4	159.4	162.4	167.1	162.8	165.6	167.0
24	182.3	170.5	175.6	180.3	177.6	176.0	180.3

TABLE 6. *Ratio of Adiabatic Bulk Modulus to Isothermal Bulk Modulus*

Pressure in kilobars	Ratio of pentane to 2-methylbutane						
	100–0	90–10	75–25	50–50	25–75	10–90	0–100
0	1.27	1.26	1.25	1.27	1.32	1.33	1.32
2	1.28	1.25	1.24	1.25	1.25	1.26	1.25
4	1.16	1.15	1.16	1.16	1.16	1.15	1.15
6	1.11	1.10	1.10	1.10	1.12	1.12	1.09
8	1.10	1.08	1.09	1.08	1.12	1.12	1.08
10	1.11	1.06	1.06	1.08	1.10	1.07	1.05
12	1.09	1.05	1.07	1.08	1.09	1.10	1.03
14	1.06	1.07	1.06	1.06	1.09	1.06	1.05
16	1.03	1.04	1.04	1.06	1.12	1.12	1.05
18	1.04	1.01	1.05	1.09	1.04	1.03	1.04
20	1.03	1.03	1.08	1.09	1.06	1.05	1.02
22	1.05	1.03	1.06	1.04	1.09	1.07	.99
24	1.02	1.01	1.04	1.06	1.09	1.05	.94

percent respectively; and for the five 90 pentane to 10 2-methylbutane mixture it is 2, 2, 16 and 3 percent respectively. Tables 2 through 6 and figures 3 through 6 are terminated at 24 kbar because at higher pressures the scatter of the data increases greatly. The increasing stiffness and decreasing volume of the sample with pressure cause the corrections and uncertainties due to piston-stack compression, cylinder expansion, and PETH compression to increase their effect on the measurements.

The effect of estimated uncertainty of input data on the relative uncertainty of the measured values of relative volume, velocity, adiabatic modulus, and isothermal modulus at 24 kbar is shown in table 7. The uncertainty attributed to a change of 2 percent at $p=0$ and 5 percent at $p=25$ kbar in the PETH bulk modulus also includes a small uncertainty due to using a simplified form of B_T (PETH)$=B_0+B_1P$ rather than a better representation of B_T (PETH)$=B_0+B_1P+Ce^{-0.28p}$ given in reference [13]. A source of some of the scatter between the runs shown above, and not fully taken into account in the uncertainty table, is the amount of liquid in the system when the PETH sleeve seals between the piston and the closure plate. Variation in the initial sealing results in an improper value for sample length and an improper value for the zero friction coefficient. Runs which seal very poorly are spotted and discarded; however, smaller variations contribute to scatter and to the difficulty of extrapolating to zero pressure and are partially responsible for the necessity of separate determination of the zero pressure values.

TABLE 7. *Estimated Relative Systematic Uncertainties at 24 Kilobars Due to Uncertainties in Input Data*

Uncertainty in input data	Relative uncertainty ($\Delta x/x$) of—			
	V/V_0	velocity	B_s	B_T^*
Friction coefficient........25%...	0.0019	0.0036	0.0093	0.0051
Piston-stack compression coefficient........10%...	.0062	.0032	.0007	.0474
Cylinder expansion coefficient........25%...	.0075	.0011	.0052	.0623
Starting sample length........0.27%...	.0023	.0039	.0054	.0073
Bulk modulus of PETH, 2% at $p=0$ to 5% at $p=25$ kbar........	.0118	.0080	.0155	.0348
RSS (Square root of the sum of the squares of the relative uncertainties)........	.0156	.0102	.0196	.0861

The measurement of the velocity of sound was limited by the quality of the signal. The poor impedance match between the tungsten carbide closure plate and the fluids which gives a combined coefficient for transmission, reflection, and transmission of 5.6×10^{-4} at $p=0$ improves to 2.03×10^{-2} at $p=24$ kbar. No signal could be detected after the pentane or 2-methylbutane froze. Also no satisfactory signal was present above 27 kbar in the mixtures. While these mixtures were not frozen and Piermarini et al. [14] show the glass transition to be 70 kbar for a 50 pentane 50 2-methylbutane mixture, the viscosity increase so attenuates the signal that although the impedance match is improving, the signal decreases to a less than usable magnitude.

The mixtures serve as useful high pressure fluids. Since there appears to be no reason to choose any one ratio above another in terms of compressibility or viscosity, the 50–50 mixture would appear a reasonable choice for maximum pressure use based on its high glass transition pressure.

5. References

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