Combined Low-Pressure and High-Pressure Measurements of Density and Bulk Modulus of Aviation Instrument Oil and 2-Methylbutane and Their Mixtures

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Dilatometric measurements were made on mixtures of aviation instrument oil and 2-methylbutane at low pressures. These results are combined with previous dilatometric and ultrasonic measurements at high pressures to give density, relative volume, and isothermal bulk modulus of the mixtures to pressures of 20 kilobars. The ratio of the adiabatic bulk modulus to isothermal bulk modulus for 2-methylbutane is also given.

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

1. Introduction

Pentane and 2-methylbutane (i-pentane), as well as their mixtures, are widely used as pressure-transmitting fluids [1][1] at very high pressures. Mixtures of pentane or 2-methylbutane with other fluids have been used to expand the range of hydrostatic pressure to beyond 50 kbar* [2]. Mixtures of 2-methylbutane with aviation instrument oil are used as pressure-transmitting fluids with good lubricity in the National Bureau of Standards 26 kbar piston gage.

Very little is known about the properties of these liquids and in particular their mixtures at high pressures. The density of pentane and 2-methylbutane was determined by Bridgman [3] to 9.8 kbar. In the present paper we will report on measurements of the density of mixtures of 2-methylbutane and aviation instrument oil (AIO) as a function of pressure up to their solidification region.

2. High-Pressure Ultrasonic and Dilatometric Measurements

The ultrasonic and dilatometric methods used in this laboratory for fluids at very high pressures have been described in a previous report [4] and again more extensively in reference [5]. We assume that the reader is familiar with these papers and will give only a very summary description here.
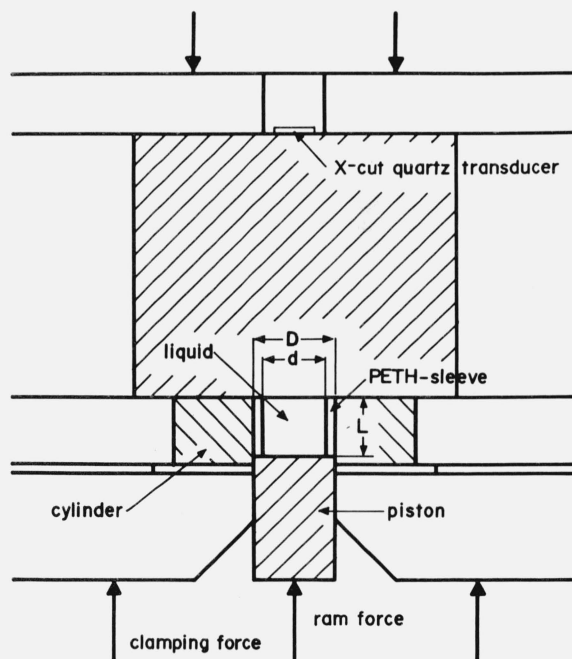

FIGURE 1. *High-pressure piston and cylinder system with fluid container.*

The high-pressure piston and die system with the polyethylene sleeve used as fluid container are shown in figure 1. Ultrasonic transit time measurements are made with the transducer cemented to the rear of the back plate. The advance of the piston into the cylinder is monitored with two dial indicators.

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[1] Figures in brackets indicate the literature references at the end of this paper.
*1 kbar = 10^8 N/m².

The volume of the fluid at pressure p can be obtained from ultrasonic measurements carried out as a function of pressure

$$V_f(p) = V_{f0} \exp\left[-(1+\alpha_p\gamma_G T)\int_0^p \frac{dp}{B_S(p)}\right] \quad (1)$$

where $V_f(p)$, V_{f0} are the volume of the fluid at pressure p and zero;

α_p is the volume expansivity at pressure p;

γ_G is the pressure-dependent Grüneisen parameter;

T is the absolute temperature; and

$B_S(p) = \dfrac{\rho(p)L^2(p)}{\tau^2(p)}$ is the adiabatic bulk modulus with $\rho(p)$ density, $L(p)$ sample length, and $\tau(p)$ ultrasonic transit time.

An iterative procedure is used to compute increasingly better approximations of $V_f(p)$ and the length $L(p)$ of the sample. The successful solution of this problem requires knowledge of $\alpha_p\gamma_G$ as a function of pressure. It also requires knowledge of the initial dimensions of the fluid container, the amount of fluid contained, and its density and speed of sound at atmospheric pressure. If $\alpha_p\gamma_G T$ is small we may choose to neglect it. For the fluids investigated here $\alpha_p\gamma_G T$ is large at atmospheric pressure and is estimated to change rapidly with pressure. Its value as a function of pressure and temperature is not sufficiently well known to be used in the present investigation. Therefore it seems more appropriate to determine the density as a function of pressure from dilatometric measurements.

Dilatometric measurements are evaluated with the following two equations:

$$V_f(p) = \frac{D^2\pi}{4} L(p)$$

$$-\frac{D^2-d^2}{4}\pi L_0\left[1-\frac{1}{B_{1,\text{PE}}}\ln\frac{B_{0,\text{PE}}+B_{1,\text{PE}}p}{B_{0,\text{PE}}}\right] \quad (2)$$

where D, d are the outer and inner diameters of the polyethylene sleeve,

L_0, $L(p)$ are the adjusted lengths of the sleeve at ambient pressure and at pressure p, respectively,

$B_{0,\text{PE}}$ is the bulk modulus of polyethylene at ambient pressure, and

$B_{1,\text{PE}} = \dfrac{\partial B_{\text{PE}}}{\partial p}$;

furthermore,

$$L(p) = L_0 + h_0 - h(p) + \phi\bar{p}_r + \eta\bar{p}_r^2$$
$$+ \gamma[1-e^{-\epsilon\bar{p}_r}] + \beta_{\text{cyl}}L_0 p \quad (3)$$

where h_0, $h(p)$ are the dial indicator readings at zero ram pressure and at pressure p;

$\phi\bar{p}_r$, $\eta\bar{p}_r^2$ are corrections for compression of the piston stack and distortion of other parts;

$\gamma[1-e^{-\epsilon\bar{p}_r}]$ is a correction for initial slack in the setup at low pressures; and

$\beta_{\text{cyl}}L_0 p$ is a correction for the effect of cylinder expansion which adjusts the actual length to the length which the sample would have in a rigid cylinder, permitting the use of $L(p)/L_0$ for V/V_0.

The coefficients ϕ, η, γ, ϵ, and β_{cyl} are determined in separate experiments described in reference [5]. The zero pressure dial indicator reading, h_0, is not known since a small unknown pressure is always generated when the press is closed up. The following procedure is used to determine h_0. A value is assumed for h_0 and the bulk modulus of the sample fluid is computed from the pressure derivative of eq (2) using $L(p)$ from eq (3). We further assume that as a first approximation the bulk modulus of a sample is a linear function of pressure, at least at low pressures. We then fit the experimental bulk modulus over part of the pressure range to a linear function of pressure.

$$B_f(p) = B_{0,f} + B_{1,f}p \quad (4)$$

from which the volume $V_f(p)$ of the fluid and the length $L(p)$ of the sample can then be computed

$$V_f(p) = V_{0,f}\left[1-\frac{1}{B_{1,f}}\ln\frac{B_{0,f}+B_{1,f}p}{B_{0,f}}\right] \quad (5)$$

$$L(p) = \frac{V_f(p)+V_{\text{PE}}(p)}{D^2\pi/4} \quad (6)$$

where

$$V_{\text{PE}}(p) = V_{0,\text{PE}}\left[1-\frac{1}{B_{1,\text{PE}}}\ln\frac{B_{0,\text{PE}}+B_{1,\text{PE}}p}{B_{0,\text{PE}}}\right] \quad (7)$$

is the volume of the polyethylene sleeve. We combine eq (3) with eqs (5), (6), and (7) and rearrange to solve for h_0

$$h_0 = h(p) - L_0$$
$$+ \frac{L_0}{D^2}\left[(D^2-d^2)\left(1-\frac{1}{B_{1,\text{PE}}}\ln\frac{B_{0,\text{PE}}+B_{1,\text{PE}}p}{B_{0,\text{PE}}}\right)\right.$$
$$\left.+ d^2\left(1-\frac{1}{B_{1,f}}\ln\frac{B_{0,f}+B_{1,f}p}{B_{0,f}}\right)\right]$$
$$- \phi\bar{p}_r - \eta\bar{p}_r^2 - \gamma[1-e^{-\epsilon\bar{p}_r}] - \beta_{\text{cyl}}L_0 p. \quad (8)$$

Now h_0 can be extrapolated from any datum point p. This procedure is unsatisfactory, at least in the present case, because the bulk modulus of the very compressible liquids is not a linear function of pressure and furthermore because in many instances the lowest pressure point is at 2000 bar and the extrapolation is rather long.

A low-pressure dilatometer was therefore constructed and measurements of $B_{0,f}$ were made to aid in the determination of h_0.

3. Low-Pressure Dilatometer

A simple low-pressure dilatometer was constructed to measure the isothermal compressibility of liquids at atmospheric pressure. The pressure vessel is shown in figure 2. The lower half is a 5-in o.d. stainless steel tube brazed to a brass bottom plate and closed at its
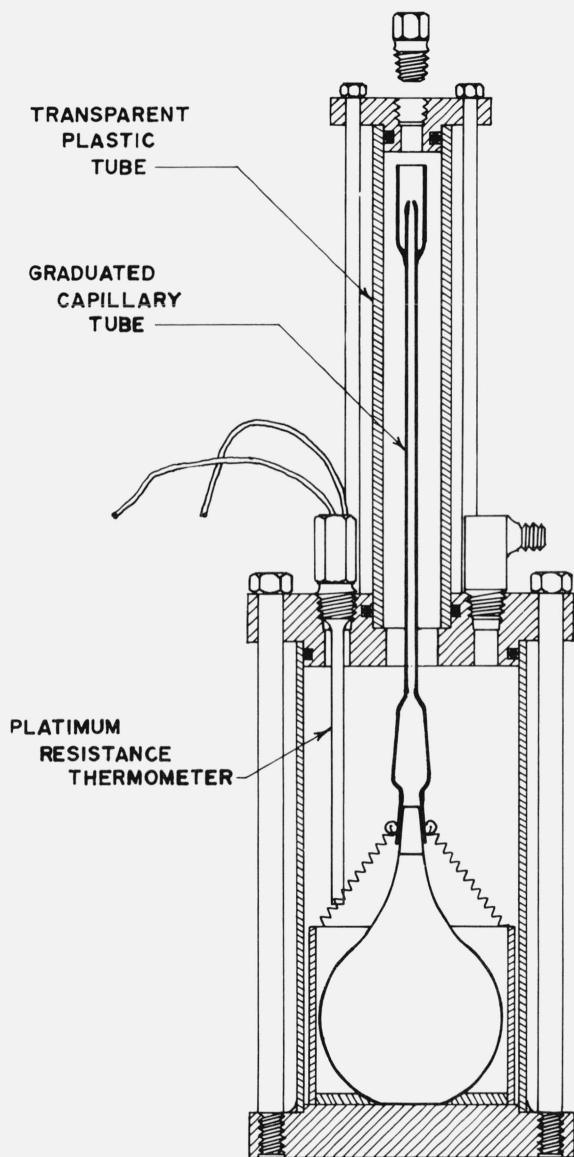

FIGURE 2. *Low-pressure dilatometer.*

upper end by a brass midplate sealed with an O-ring and held to the bottom plate by six long bolts. The midplate is drilled and tapped to receive a platinum resistance thermometer and a flare fitting for the pressure

tap. In addition the midplate holds a transparent plastic tube into which the capillary of the dilatometer protrudes. This plastic tube is sealed by O-rings and held to the midplate by bolts from a top closure.

The dilatometer is made from a 500-ml round-bottom flask sealed to the male portion of a ground-glass taper joint. A 0.2-ml graduated pipet was sealed to the female portion of the ground-glass taper joint. The upper end of the pipet has an open cup sealed around it to aid in the final filling. When assembled the readable portion of the scale on the pipet covers approximately 0.17 ml, graduated in 0.001 ml. The flask is nested in a perforated brass can with springs attached to the rim which hook over a clamp around the ground-glass joint of the pipet to hold the joint together. The can also serves to locate the dilatometer in the pressure vessel.

The base plate of the pressure vessel was maintained slightly above room temperature to permit thermostatic control of the temperature. The same fluid used in the dilatometer was also used as a bath fluid to fill the pressure vessel around the dilatometer to about one inch below the midplate. The same fluid was chosen to decrease evaporation from the open capillary and to cause similar changes in temperature due to change in pressure. Nitrogen was used above the liquid as the pressure fluid.

The volume of the dilatometer was determined to within 0.2 percent by the weight of water contained in it. The capillary scale was checked with a weighed slug of mercury and was found to be within 0.2 percent of the capillary volume and uniform to within 0.2 division. The pressure was measured with a calibrated bourdon tube gage. The temperature of the liquid surrounding the dilatometer within the pressure vessel was measured with a platinum resistance thermometer.

After filling the apparatus with a sample of fluid, the position of the meniscus in the capillary was read at various temperatures and at pressures between 1 and 5 bars.

The data were fitted to eq (9) by OMNITAB FIT for V_{f0}, K_f, α_f.

$$V_{D0} + V_{D0}\alpha_g(t - t_0) - V_{D0}K_g(P - P_0) + V_c$$
$$= V_{f0} - V_{f0}K_f(P - P_0) + V_{f0}\alpha_f(t - t_0) \qquad (9)$$

where

V_{D0} is the volume of the dilatometer at P_0 and t_0,
α_g is the volumetric thermal coefficient of the glass,
K_g is the compressibility of the glass,
V_c is the reading of the fluid level in the capillary at P, t,
P is the pressure,
t is the temperature,
P_0 is standard atmospheric pressure,
t_0 is an assigned reference temperature near room temperature,
V_{f0} is the volume of fluid at P_0, t_0,
K_f is the compressibility of the fluid, and
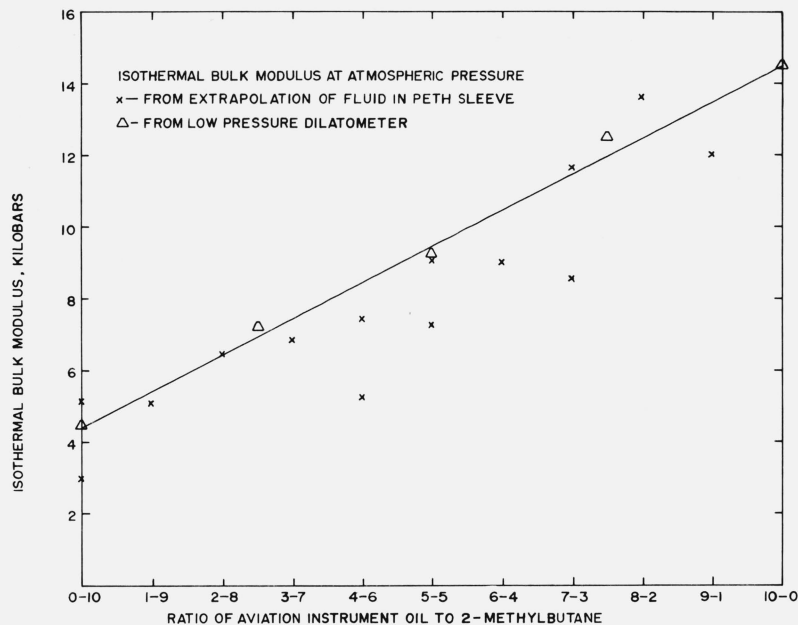α_f is the volumetric thermal coefficient of the fluid.

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FIGURE 3. *Isothermal bulk modulus of mixtures of 2-methylbutane (i-pentane) and aviation instrument oil at atmospheric pressure.*

The estimated systematic uncertainties in the measurements of K_f are 0.2 percent due to V_{D0}; 1 percent for α_g and K_g; 0.3 percent for p; 0.2 percent for V_c; and 3 percent for t. The largest uncertainty, the 3 percent for t, results from an estimated uncertainty of 0.02 °C in the measurement of the equilibrium temperature. While this method of measuring the isothermal compressibility at atmospheric pressure gives results good only to about 3 percent, this is sufficient for our present use. The results for 2-methylbutane, aviation instrument oil, and 50/50, 75/25, and 25/75 mixtures of the two are shown in figure 3 by (Δ) as the isothermal bulk modulus at atmospheric pressure ($B_{0,f}^{L}$).

4. Results

Evaluation of the experimental data requires the determination of h_0 from eq (8). For this purpose and in spite of the slight nonlinearity, the bulk modulus values

$$B_f(p_m) = \frac{(p_{n+1} - p_n)V_{f0}}{V_f(p_n) - V_f(p_{n+1})} \quad (10)$$

with

$$p_m = \frac{p_n + p_{n+1}}{2}$$

were fitted to

$$B_f(p) = B_{0,f} + B_{1,f}p$$

for the first six non-zero pressures (approximately 1 to 10 kbar) for each fluid sample. The resulting $B_{0,f}$

are plotted (x) in figure 3 and both coefficients are listed in table 1. A considerable improvement can be made, if $B_{0,f}$ is set equal to $B_{0,f}^{L}$, the zero-pressure bulk modulus obtained from the low-pressure dilatometer measurements. A straight line is fitted to the same $B_f(p_m)$ as used above and forced through $B_{0,f}^{L}$. The $B_{0,f}^{L}$ are also plotted (Δ) in figure 3 and the coefficients $B_{0,f}^{L}$ and $B_{1,f}^{F}$ are listed in table 1. The values of $B_{0,f}^{L}$ and $B_{1,f}^{F}$ for each mixture were used to obtain an

TABLE 1. *Density at atmospheric pressure and coefficients of bulk modulus of mixtures of aviation instrument oil and 2-methylbutane*

Ratio of aviation instrument oil to 2-methylbutane	ρ_0	$B_{0,f}$	$B_{1,f}$	$B_{0,f}^{L}$	$B_{1,f}^{F}$
	g/cm^3	kbar		kbar	
0–10	0.615	2.99	11.54	4.5	11.27
0–10	.615	5.13	11.14	4.5	11.26
1–9	.651	5.07	11.24	5.5	11.16
2–8	.678	6.43	10.96	6.5	10.95
3–7	.705	6.82	10.99	7.5	10.87
4–6	.730	7.43	11.18	8.5	10.99
5–5	.752	7.25	11.69	9.5	11.30
5–5	.752	9.09	11.75	9.5	11.68
6–4	.781	8.98	11.37	10.5	11.11
7–3	.807	11.68	11.36	11.5	11.39
8–2	.827	13.61	11.21	12.5	11.40
9–1	.851	12.00	11.14	13.5	10.88
10–0	.879	10.41	12.10	14.5	11.28

h_0 from eq (8) by averaging the values of h_0 from the first six non-zero pressure points for each mixture.
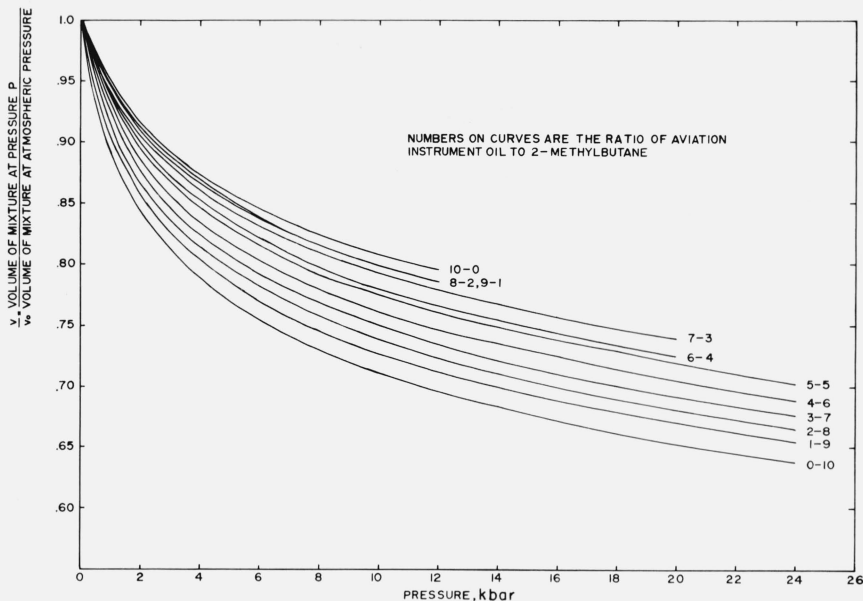
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FIGURE 4. *Ratio of volume at pressure to volume at atmospheric pressure as a function of mixture and pressure.*

These values of h_0 are used in eq (3) for $L(p)$. $L(p)$ is used in eq (2) to determine $V_f(p)$. Figure 4 shows $V_f(p)/V_{f0}$ (or ρ_0/ρ) for each mixture. The values for $V_f(p)/V_{f0}$ are given in table 2.

Table 3 shows the values of the isothermal bulk modulus for each mixture at various pressures. The values at atmospheric pressure are obtained from a linear fit to the values of the low-pressure dilatometric data. All other values are from linear interpolation between nearest experimental values. The tabulated data were fitted to $B_T^*(m, p) = A + Bm + Cm^2 + Dp + Emp + Fm^2p + Gp^2 + Hmp^2 + Im^2p^2$. The variable m is the fraction of aviation instrument oil in the mixture of the oil and 2-methylbutane and p is the pressure. The results indicated that an acceptable fit for the accuracy

of this data could be obtained with just the terms A, Bm, Dp, Emp, and Gp^2. A fit was made for these variables and the result is:

$$B_T^*(m, p) = 4.542 + 9.568\,m + 8.735\,p + 1.471\,mp$$
$$- .06348\,p^2 \qquad (11)$$

for B_T^* and p in kilobars. These results are shown in figure 5.

The adiabatic bulk modulus for 2-methylbutane was computed from ultrasonic measurements of the time of flight and the dilatometric measurements of density and length of sample. The ratio of the adiabatic bulk modulus (B_S) to the isothermal bulk modulus (B_T^*)

TABLE 2. *Ratio of* V/V_0

Pressure in kilobars	Ratio of aviation instrument oil to 2-methylbutane										
	0–10	1–9	2–8	3–7	4–6	5–5	6–4	7–3	8–2	9–1	10–0
0.5	0.930	0.940	0.954	0.958	0.962	0.966	0.966	0.970	0.971	0.974	0.976
1	.893	.903	.911	.920	.926	.934	.938	.941	.944	.949	.952
2	.843	.856	.866	.876	.885	.893	.898	.905	.909	.912	.919
3	.811	.825	.836	.846	.856	.866	.871	.879	.885	.887	.893
4	.788	.803	.814	.824	.835	.846	.851	.860	.866	.868	.874
6	.754	.770	.781	.792	.803	.814	.821	.831	.838	.838	.845
8	.730	.746	.757	.768	.779	.791	.798	.809	.816	.816	.824
10	.711	.727	.738	.749	.761	.774	.780	.792	.799	.798	.807
12	.696	.712	.722	.734	.747	.760	.766	.779	.786	.784	.796
14	.684	.700	.710	.721	.734	.750	.754	.767			
16	.672	.689	.700	.710	.724	.737	.743	.756			
18	.662	.679	.690	.701	.714	.728	.733	.747			
20	.653	.670	.681	.692	.705	.719	.724	.738			
22	.645	.662	.672	.684	.697	.711					
24	.638	.654	.665	.676	.689	.703					

as a function of pressure for 2-methylbutane is shown in figure 6. The value 1.33 plotted at atmospheric pressure is the ratio of B_S/B_T^* obtained from data from the International Critical Tables [6].

TABLE 3. *Isothermal bulk modulus* $(-V\,dp/dV)$ *in kilobars*

| Pressure in kilobars	Ratio of aviation instrument oil to 2-methylbutane										
	0–10	1–9	2–8	3–7	4–6	5–5	6–4	7–3	8–2	9–1	10–0
0	4.5	5.5	6.5	7.5	8.5	9.5	10.5	11.5	12.5	13.5	14.5
2	22.2	23.8	24.4	25.8	26.0	27.5	28.6	30.9	33.8	31.2	22.3
4	37.9	40.1	40.6	41.6	43.1	45.3	46.4	49.6	50.4	48.7	50.2
6	54.3	56.1	58.2	59.1	60.0	62.2	63.0	66.4	69.0	67.6	69.1
8	70.0	70.7	70.5	72.1	75.6	80.3	79.8	82.8	83.8	81.8	88.5
10	88.9	86.6	86.1	90.9	97.9	98.9	103.8	114.1	112.5	103.6	118.6
12	102.1	112.0	106.5	106.0	113.3	122.3	115.5	124.6	133.3	127.2	162.4
14	113.2	122.8	125.1	124.4	127.3	129.8	125.4	133.7			
16	122.2	130.6	140.6	139.1	141.2	149.3	147.7	148.7			
18	138.2	144.6	147.5	149.7	153.5	157.2	157.8	164.4			
20	153.8	149.3	158.9	173.6	165.5	172.3	165.5	173.0			
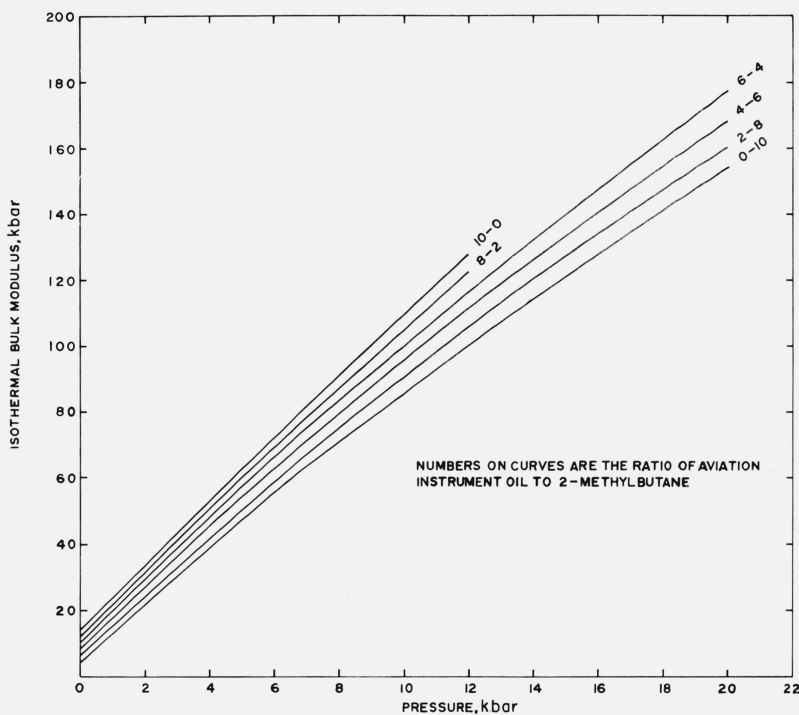
FIGURE 5. *Smoothed values of isothermal bulk modulus* $(B_T^* = -V\,dp/dV)$ *as a function of mixture and pressure.*
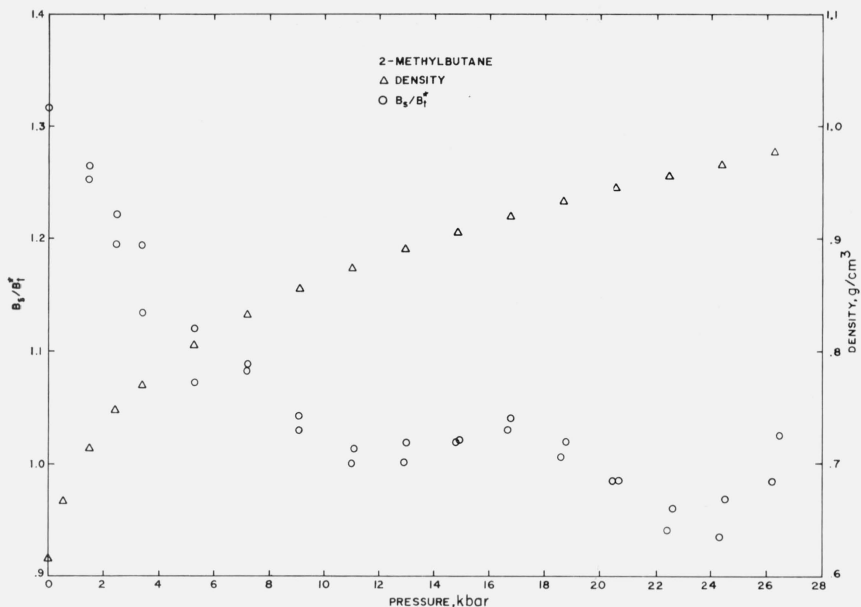
FIGURE 6. *Density and the ratio of adiabatic bulk modulus to isothermal bulk modulus of 2-methylbutane as a function of pressure.*

5. Conclusions

The use of a low-pressure dilatometer for measurement of isothermal bulk modulus of various liquids has proved useful in fitting data obtained in our high-pressure piston and die with polyethylene fluid container. This has resulted in more usable values for the bulk modulus and relative volumes of the liquids at high pressure.

6. References

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