Densities of Liquid Polymers at High Pressure. Pressure–Volume–Temperature Measurements for Polyethylene, Polyisobutylene, Poly(vinyl acetate), and Poly(dimethylsiloxane) to 1 kbar

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ABSTRACT: Volumetric data are reported for low-density polyethylene, polyisobutylene, poly(vinyl acetate), and poly(dimethylsiloxane) in the region 25–200° and at pressures to 1 kbar. Experimental results are confined to the amorphous liquid state. Tait-equation coefficients are given to represent the smoothed PVT data.

While accurate measurements of volumetric properties of common liquids have been reported over the last 20 years,[1–5] such measurements are scarce for polymeric liquids at high temperatures and pressures.

Quach and Simha[6] measured densities of polystyrene (PS) and poly(*o*-methylstyrene) in the region 1–2000 bars and 10–200°. Goldstein and McKinney[7] measured the density of poly(vinyl acetate) (PVAC) in the region 1–800 bars and −35 to 100°. Hellwege[8] reported volumetric data for polyethylene (PE), poly(vinyl chloride) (PVC), and poly(methyl methacrylate) (PMMA). Maloney and Prausnitz[9] compared density data for PE from different sources and found appreciable disagreement. Volumetric data for polyisobutylene (PIB) and poly(dimethylsiloxane) (PDMS)[10,11] are confined to modest pressures (1–40 bars) and those for PVC and PMMA are confined to a small temperature range (120–140° for PMMA and 90–100° for PVC).

This work presents experimental results at advanced pressures for four polymers (low-density PE, PVAC, PIB, and PDMS) in the temperature region 25–200° and at pressures from 1 to 1000 bars. All experimental work reported here is confined to the amorphous liquid state.

Apparatus

Most high-precision volumetric data for compressed liquids have been obtained using a flexible bellows to contain the sample and to isolate it from the pressure-transmitting fluid.[1,2,6] This method was also used here. The liquid with confining fluid is sealed in the metal bellows. Pressure is applied by hydraulic oil causing the bellows to contract until the pressure of the sample inside the bellows balances the applied pressure; the volume change is obtained from measuring the change in length of the bellows. The displacement of the bellows is obtained by following the motion of a magnetic core with a linear, variable differential transformer, and by measuring the displacement with a micrometer slide with an accuracy of ±1 μ. The bellows assembly is calibrated to determine the exact area of the bellows and the contraction of the stainless-steel parts as a function of temperature and pressure. For calibration, we used mercury and heptane because reliable PVT data exist for these fluids.[1,2,5,6] The calibration shows that the bellows area is independent of pressure in the range 1–1000 bars. While the contraction of the stainless-steel parts is a function of pressure, it is independent of temperature since the compressibility of stainless steel does not change appreciably as the temperature varies from 25 to 200°. Details of the calibration are presented elsewhere.[12]

The stainless-steel pressure cell has an inside diameter of 2.54 cm and an outside diameter of 11.5 cm. The bellows from Robert Shaw Co., Tenn., has an effective inside diameter of 1.23 cm and an effective length of 2.54 cm. The bellows and the pressure cell are located in a high-temperature bath with silicone oil as the heating fluid. The bath is controlled to ±0.01° by a Hallikainen proportional temperature controller. At temperatures close to 200°, however, variations in the temperature of the bath increase to ±0.1°. Calibrated thermometers were used for temperature measurements whose accuracy is estimated to be ±0.1°.

Pressures are measured with a precision Heise gauge covering the range 1–1000 bars. The accuracy of the pressure gauge is 0.1% of the full scale (±1 bar).

All measurements were conducted under isothermal conditions. Pressure was raised approximately 100 bars for each measurement. To investigate the possible existence of hysteresis in the apparatus, additional experiments were made with PIB. The pressure was raised to 1000 bars and then data were obtained at decreasing pressures. Since the volumetric data obtained with decreasing pressure did not differ (within experimental error) from those obtained with increasing pressure, we conclude that hysteresis effects are negligible.

Procedure and Materials

Bellows are filled with approximately 50 vol % polymer and 50 vol % mercury under high vacuum to avoid entrapment of gas bubbles. The presence of mercury was necessary to prevent mechanical damage to the bellows when studying a highly viscous polymer, especially at low temperatures. The total volume available is approximately 11 cm^3.

Characteristics of polymer samples are shown in Table I.

The bellows apparatus yields only the change in volume of the sample in the bellows relative to that at atmospheric pressure. Therefore it is necessary to measure independently V_0, the specific volume of the polymer at atmospheric pressure. Accurate measurements by Flory and coworkers[10,11] were used for atmospheric pressure density data for PIB and PDMS. For PE, PVAC, and Hg, density data in ref 13 through 18 were used.

The apparatus was calibrated with PVT data for mercury and with heptane density data at 22.8°. To test the accuracy of the experimental method, experimental results for heptane were compared with data reported by Boelhouwer,[1] Weale,[5] and Doolittle[2] at 30°. Maximum deviation in relative volume was ±0.17% (Doolittle), ±0.14% (Weale), and ±0.20% (Boelhouwer).

Taking into consideration errors in pressure and temperature measurements as well as errors in the heptane and mercury data used for calibration, the overall uncertainty of our relative volume measurements is 0.04% at tempera-

Table I
Polymer Characteristics

Polymer and source	$\bar{M}_n$[a]	$\bar{M}_w$[b]	$\bar{M}_v$[c]	$\bar{M}_w/\bar{M}_n$	Other characteristics
PE, Union Carbide DXM-195	2.5×10^4	1.9×10^5		7.6	Melt index = 5.7 dg/min; contains some small amount of 2-propanol as chain transfer agent; sp. gravity ≈ 0.92 at 25°
PIB, Enjay Vistanex-LM			3.6×10^4		Contains negligible amounts of ash; molecular weight distribution is narrow; sp. gravity ≈ 0.92 at 25°
PVAC, Cellomer Associates	84,000	330,000		3.92	
PDMS, Cellomer Associates 145C-02	47,200	166,000		3.53	

[a] $\bar{M}_n$ = number-average molecular weight. [b] $\bar{M}_w$ = weight-average molecular weight. [c] $\bar{M}_v$ = viscosity-average molecular weight.

Table II
Data Summary[a]

Polymer	Pressure range, bars	Temperature range, °C	No. of isotherms
PE	1–1000	140–200	4
PIB	1–1000	52.8–110	5
PDMS	1–1000	24.9–69.9	6
PVAC	1–1000	64–120	6

[a] Complete data are available elsewhere.[12]

Table III
Parameters for Tait Equation

Polymer	$C \times 10^2$	$b_1 \times 10^{-3}$, bars	$b_2 \times 10^{+3}$, °C^{-1}	$\sigma \times 10^4$[a]
PIB	8.7132	1.9067	4.1458	2.76
PDMS	10.0916	1.0407	5.8507	6.18
PVAC	10.4623	2.2308	3.4315	3.37
PE	9.6959	1.9873	5.0976	7.69

[a] σ is the root-mean-square deviation of the relative volume as calculated from Tait's equation.

tures below 150° and 0.06% at higher temperatures. Detailed error analysis is given elsewhere.[12]

Results and Discussion

Relative volumes were measured for PE, PIB, PVAC, and PDMS as a function of pressure and temperature over the range shown in Table II. Complete original data are available elsewhere.[12] Figure 1 shows some of the isotherms.

The Tait equation is suitable for smoothing the data and for interpolation with respect to temperature and pressure. Different forms of the Tait equation have been used to represent the PVT behavior for a number of liquids, including polymeric liquids.[3,5,6,9] The Tait equation used here is

$$V/V_0 = 1 - C \ln (1 + P/B) \tag{1}$$

where V = specific volume at pressure P and temperature T; V_0 = specific volume at P = 1 bar, and at the same temperature T; C = dimensionless constant; B = temperature-dependent constant with units of pressure. Simha et al.[13,16] have shown that the temperature dependence of B can be expressed by

$$B = b_1 \exp(-b_2 T) \tag{2}$$

where b_1 and b_2 are empirical constants. Substituting (2) into (1)

$$V/V_0 = 1 - C \ln \left\{ 1 + \frac{P}{b_1 \exp(-b_2 T)} \right\} \tag{3}$$

For high molecular weight hydrocarbons and for several polymers, dimensionless constant C in eq 3 is set equal to 0.0894 by Weale[5] and by Simha.[6] However, we have allowed this constant to vary from one polymer to another.

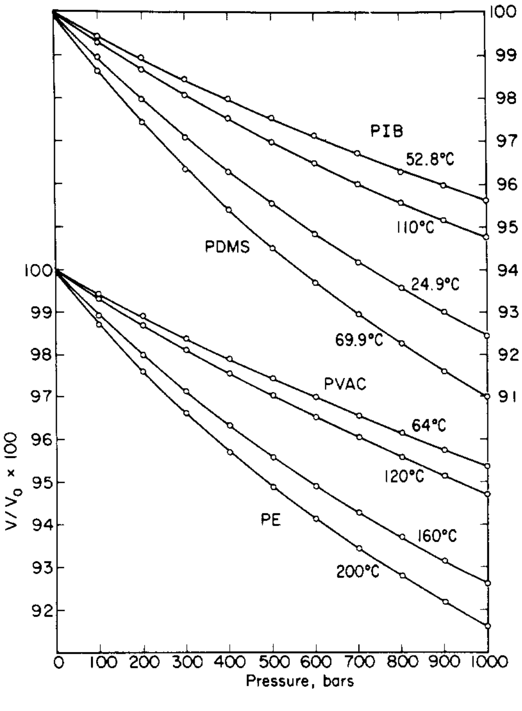

Figure 1. Relative volumes of polyisobutylene, poly(dimethylsiloxane), poly(vinyl acetate), and polyethylene at selected temperatures.

The three parameters C, b_1, and b_2 were evaluated from the experimental PVT data by least-squares regression.

Table III presents a summary of the results. In addition to the constants, Table III also gives the root-mean-square deviation between the fit and the experimental data. Equa-

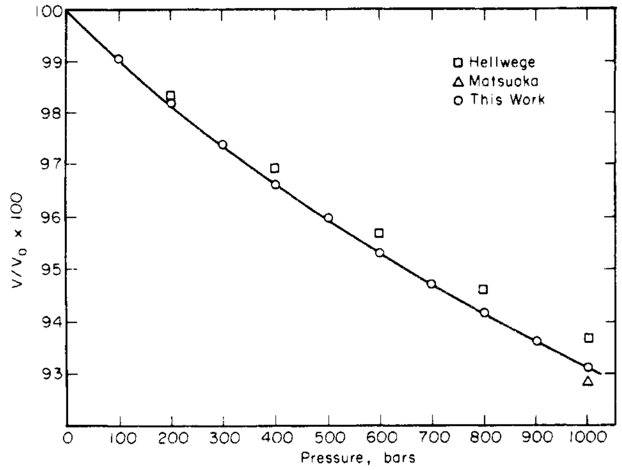

Figure 2. Comparison of polyethylene density at 140°.

tion 3 is able to represent all our data within experimental accuracy.

The three-parameter Tait equation represents the data with appreciably better accuracy than the two-parameter Tait equation (with $C = 0.0894$), especially for polyethylene and for poly(dimethylsiloxane). For these polymers, the root-mean-square deviation with the two-parameter Tait equation is approximately twice that obtained with the three-parameter Tait equation and therefore larger than our estimated experimental uncertainty. For poly(vinyl acetate) and polyisobutylene, the two-parameter Tait equation can represent our data almost within experimental uncertainty but with larger root-mean-square deviations than those shown in Table III.

Comparison of Experimental PVT Data

To our knowledge, no high-pressure density data have been reported previously for PIB and PDMS in the temperature range indicated in Table II. However, low-pressure data are available for these polymers.[10,11]

Figure 2 shows a comparison between our PE data at 140° and those in the literature.[8,17] Data by Hellwege and coworkers[8] are at 140.5°. The deviation is about ±0.5% at 1000 bars.

Goldstein and McKinney[7] reported accurate density data for PVAC in the region 1–800 bars and −35–100°. McKinney and Simha[13] interpolated these data to other temperatures and pressures using the Tait equation. We compare in Table IV our measured relative volumes (smoothed) at 64 and 95.8° with those calculated by using the Tait equation with coefficients reported in ref 13.

We made no attempt in this work to review and test the different equations of state for polymer liquids. The Tait equation is used only for data representation. However, in a forthcoming publication we consider a new equation of state for fluids containing small or large molecules and we compare it with previously proposed equations of state for liquid polymers.

Table IV
Comparison of Smoothed PVAC Data

		$V/V_0 \times 10^4$	
T, °C	P, Bars	McKinney	This work
64	100	9944	9943
	200	9892	9889
	400	9795	9789
	600	9707	9698
	800	9628	9614
95.8	100	9936	9937
	200	9877	9877
	400	9769	9767
	600	9672	9668
	800	9585	9577

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Supplementary Material Available. Tables for experimental relative volumes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24X reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number MACRO-75-536.

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