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Determination of the Equation of State of Polyisobutylene

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ABSTRACT: The density, thermal expansion coefficient, and thermal pressure coefficient for polyisobutylene of mol wt 40,000 have been accurately determined from 0 to 150°. Results are compared with the reduced equation of state employed in the theory of solutions. The characteristic parameters v^*, T^*, and p^* required for the treatment of polyisobutylene solutions are obtained from the experimental results.

The present investigation was undertaken with the primary object of furnishing the equation-of-state data required for interpretation of the thermodynamic properties of polyisobutylene (PIB) solutions.[1,2] Over small ranges of pressure and temperature the equation of state is specified by the density ρ (or the specific volume v_{sp}), the coefficient of thermal expansion α, and the thermal pressure coefficient γ, each determined at the reference temperature and pressure (*e.g.*, at $p \cong 0$). These quantities serve for the evaluation of characteristic parameters v^*, p^*, and T^* as described in the preceding paper[1] and elsewhere.[3-5] The latter parameters scale the reduced equation of state. They also enter directly into the theoretical relationships[3,6] for the excess properties of mixtures, accurate values of the parameters v^*, p^*, and T^* for each component being required.

The equation-of-state characteristics of bulk amorphous polymers are of intrinsic interest apart from their utility for the analysis of properties of solutions. These substances constitute an important class of liquids characterized by low coefficients of thermal expansion and of compressibility. Correlation of the properties of polymeric liquids with theories of the liquid state presents an obvious challenge. With these several considerations in mind, we have determined the α and γ for PIB over a wide range of temperature, 0–150°, and with accuracy commensurate with similar determinations on low molecular liquids.

Experimental Section

Polyisobutylene (Enjay Vistanex LMMS) was fractionated from a 1% solution in benzene at 28° using methanol as the precipitant. The first fraction was discarded and a large (40 g) second fraction (estimated $\bar{M}_v = 4 \times 10^4$) was used for all subsequent measurements. The precipitant was added slowly to ensure that large amounts of low molecular weight material would be eliminated.

Dilatometers, pressure cells, and experimental procedures for determining α and γ have been described in detail elsewhere.[7] For each series of measurements, dilatometers or pressure cells were charged with weighed quantities of polymer, after which they were thoroughly degassed for 24 hr

at *ca.* 100° under a vacuum of 10^{-5} torr. Temperatures constant to $\pm 0.002°$ were maintained in liquid (water or silicone oil) thermostat baths operating from 6 to 200°.

The absolute density of PIB was measured by placing a weighed sample of *ca.* 7.5 g in a dilatometer of calibrated volume, with mercury serving as the confining fluid. The weight of the dilatometer and contents gave the quantity of mercury, in addition to polymer, occupying the calibrated volume at the chosen temperature. The density of PIB thus determined is $\rho = 0.9134 \pm 0.0001$ g cc^{-1} at 32.000 $\pm 0.005°$. Densities at all other temperatures were referred to this value.

Thermal expansion coefficients were determined using weighed samples of *ca.* 25 g of polymer placed in larger dilatometers of uncalibrated volume. The weight of mercury expelled from the dilatometer on raising the temperature, or taken in on cooling, yielded relative densities at various temperatures with high accuracy.

Thermal pressure coefficients were determined by the methods of Allen, Sims, and Wilson[8] as modified by Orwoll.[7] Samples of *ca.* 25 g were used.

Results

Relative densities were determined at intervals of about 4° throughout the temperature range 6–200°. Three series of measurements were carried out using separate samples of PIB. The closely agreeing results from the three sets of measurements were converted to absolute densities on the basis of the measurement at 32° reported above. They were fitted by the method of least squares to the quadratic equation

$$\rho = 0.9297 - 5.123 \times 10^{-4}t + 6.15 \times 10^{-8}t^2 \text{ g cc}^{-1} \tag{1}$$

which is accurate to $\pm 1 \times 10^{-4}$ g cc^{-1} in the range 0–150°; the temperature t is in degrees Centigrade. Exposure of the PIB sample in the dilatometer to temperatures in excess of *ca.* 150° caused the densities subsequently measured at lower temperatures to fall below those determined before. These observations are indicative of degradation at temperatures above 150°. Densities were accurately reproducible upon cooling if the heating cycle did not include temperatures over 150°.

The thermal expansion coefficient derived from eq 1 is (deg^{-1})

$$\alpha = 5.51 \times 10^{-4} + 1.71 \times 10^{-7}t \tag{2}$$

The latitude of error increases nearly linearly with temperature from $\pm 0.2\%$ at 25° to $\pm 1.2\%$ at 150°.

(1) P. J. Flory, J. L. Ellenson, and B. E. Eichinger, *Macromolecules*, **1**, 279 (1968).
(2) B. E. Eichinger and P. J. Flory, *Trans. Faraday Soc.*, in press.
(3) P. J. Flory, *J. Amer. Chem. Soc.*, **87**, 1833 (1965).
(4) A. Abe and P. J. Flory, *ibid.*, **87**, 1838 (1965).
(5) B. E. Eichinger and P. J. Flory, *Trans. Faraday Soc.*, in press.
(6) P. J. Flory, R. A. Orwoll, and A. Vrij, *J. Amer. Chem. Soc.*, **86**, 3507, 3515 (1964).
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(8) G. Allen, D. Sims, and G. J. Wilson, *Polymer*, **2**, 375 (1961).

Table I

t, °C	v_{sp}, cc g⁻¹	$\alpha \times 10^4$, deg⁻¹	γ, bars deg⁻¹	$\tilde{v}$	v_{sp}^*, cc g⁻¹	T^*, °K	p^*, cal cc⁻¹
0	1.0756	5.51	12.66	1.1366	0.9463	7430	107
25	1.0906	5.55	11.36	1.1488	0.9493	7577	107
50	1.1059	5.60	10.19	1.1610	0.9525	7726	106
100	1.1376	5.68	8.23	1.1854	0.9597	8029	103
150	1.1706	5.77	6.78	1.2092	0.9681	8338	100

Thermal pressure coefficients were determined at intervals of about 25° from 10 to 172°. Each isobar was established by measuring the pressure as a function of temperature at four or five points within the pressure range 7–35 bars. The change of pressure with temperature was accurately linear; slopes, representing γ, were therefore unambiguously defined. The equation

$$\gamma = 12.66 - 5.45 \times 10^{-2}t + 1.02 \times 10^{-4}t^2 \text{ bars deg}^{-1} \tag{3}$$

deduced by the method of least squares represents the results with an accuracy of ± 0.06 bar deg⁻¹. The determination at the highest temperature gave no evidence of vitiation due to degradation.

Values of $v_{sp} = \rho^{-1}$, α, and γ at the temperatures specified in Table I were obtained from the empirical equations given above. They are listed in the second, third, and fourth columns, respectively. The reduced volumes $\tilde{v}$ given in the fifth column were calculated from α according to eq 6 of the preceding paper.[1] Reduced temperatures $\tilde{T}$ and reduced pressures $\tilde{p}$ (neither having been included in Table I) were calculated from $\tilde{v}$ using eq 5 and 7 of that paper. The characteristic parameters v_{sp}^*, T^*, and p^* given in the last three columns of Table I were calculated according to eq 2–4 of the preceding paper.

The variation of v^* with temperature, i.e. $(1/v^*)(dv^*/dT)$, amounts to about 15% of α. This deviation of v^* from constancy is about the same as has been observed for low molecular liquids.[4] The change of p^*

over a range of 150° is small, and is not much outside experimental uncertainty.

The theory may be put to further test by analysis of the quantities $d\alpha/dT$ and $(d\gamma/dT)_{p=0}$. From eq 6 of the preceding paper,[1] it is easily shown[6] that

$$d\alpha/dT = (7 + 4\alpha T)\alpha^2/3 \tag{4}$$

which yields the result $d\alpha/dT = 7.7 \times 10^{-7}$ deg⁻². The experimental value, 1.7×10^{-7} deg⁻², is very much smaller; the discrepancy is much larger than observed for low molecular weight liquids.[4,7]

According to eq 4 and 5 of the preceding paper

$$(d\gamma/dT)_{p=0} = -(\gamma/T)(1 + 2\alpha T) \tag{5}$$

with p^* and v^* treated as constants. From the values of α and γ at 0°, we obtain -5.99×10^{-2} bars deg⁻² for this coefficient, in good agreement with the experimental value of -5.45×10^{-2} bars deg⁻².

The poor agreement between calculated and observed values of $d\alpha/dT$ reflects both the large uncertainty in the experimental value of $d\alpha/dT$ ($\sim \pm 30\%$) and aberrations in theory at once apparent in the nonconstancy of v^*. The small variation of p^* with temperature and the close agreement between calculated and observed values of $(d\gamma/dT)_{p=0}$ are interrelated. They will be found on close examination to support the validity of theoretical approximations[3,5,6] to the intermolecular energy.