Volume Changes of Mixing and Excess Coefficients of Thermal Expansion for Solutions of Polymethylene in *n*-Decane

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ABSTRACT: Excess volumes of mixing have been measured for mixtures of polymethylene in *n*-decane between 135 and 175°. Volumes of the pure components were observed to decrease on mixing by 1.5% or less. The measured excess volumes and their temperature coefficients are in good agreement with values calculated using the model of Flory. A small departure from Brønsted's principle of congruence was detected.

Of the various equilibrium properties of polymer solutions, the volume change of mixing has received comparatively little attention. Traditional polymer solution theory[1,2] ignores any change in total volume when solvent and polymeric solute are mixed. Only with the advent of more sophisticated treatments[3,4] which purport to account for such volume changes, has there been a significant interest in studying these properties of polymer solutions.

On the other hand, the volume change accompanying mixing of two low molecular weight liquids has been the object of study for many years. Some of the most careful measurements have been made on binary systems of *n*-alkanes.[5-9] Without exception these hydrocarbons have been found to contract on mixing. The magnitude of the effect increases with increasing temperature and also with increasing disparity in the lengths of the components.

There have also been a number of theoretical studies of this property. Some[7,10-12] treat the volume changes of mixing of alkane systems in terms of a corresponding states model; another[4,13] assumes a partition function for liquid solutions; and others[5,6,9,12,14-16] are applications of the Brønsted's principle of congruence.[17]

It is the object of this study to extend the volumetric measurements of binary solutions of *n*-alkanes to include a polymeric component, *viz.*, polymethylene (PM), and to assess the ability of the model of Flory[4] to account for the volumetric behavior of these solutions. Here we report our studies of the volume change of mixing for the system polymethylene + *n*-decane and its temperature coefficient.

Experimental Section

Materials. Marlex 6002 linear polyethylene, kindly supplied by DeBell and Richardson, Inc., was used without fractionation. Its number-average molecular weight was *ca.* 1.4 × 10⁴. The *n*-decane used was the Research Grade (99.49%) of Phillips Petroleum. Both components were thoroughly degassed before use.

Method. The procedure followed was the dilatometric method of Eichinger and Flory.[18,19] The two components were contained in a glass cell, separated from each other by mercury which completely filled the rest of the container. The tip of a capillary tube which was the only opening to the cell was immersed in an external reservoir of mercury contained in a weighing bottle. As the temperature of the cell was raised, mercury was expelled from the cell into the weighing bottle; on cooling mercury was drawn from the bottle into the cell. The mass of mercury remaining in the external reservoir was measured at 2–3° intervals over the range *ca.* 135–175° and was fitted to a polynominal equation, cubic in temperature.

The two components were then mixed by tilting the cell so that decane flowed into the compartment containing the polymethylene. The mass of the weighing bottle was again determined as a function of temperature over the same range and again fitted to a cubic equation. The volume change on mixing was computed directly as the ratio of the change in the mass of the weighing bottle to the density of mercury.

Temperatures were measured using either a Hewlett-Packard Model 2801A quartz thermometer or a Leeds and Northrup Model 8160 platinum resistance thermometer with a Honeywell Model 1551 Mueller bridge.

Results

The observed relative volume changes, V^E/V^0, are presented in Table I. Here V^E is the measured change and V^0 represents the combined volumes of the two components before mixing. These ratios have been interpolated for 140, 150, 160, and 170°. Their uncertainties do not exceed ±2%.

These measured volume charges are substantially larger in magnitude than ones reported for mixtures of low molecular weight *n*-alkanes. They are also larger than most excess volumes observed for other polymer systems.[20]

Excess coefficients of thermal expansion

$$\alpha^E = \frac{1}{V}\left(\frac{\partial V^E}{\partial T}\right)_p \tag{1}$$

have been determined by differentiating analytical expressions for the observed volume changes as a function of temperature. Coefficients evaluated at four temperatures are listed in Table II. The uncertainties in these quantities are *ca.* ±15%. At its minimum at 150° α^E is approximately 14% less than the thermal expansion coefficient of the solution.

Theoretical Expressions. The zero-pressure isobar for solutions of polymethylene in decane can be written in reduced form according to a model proposed by Flory.[4,19]

$$\tilde{T} = (\tilde{v}^{1/3} - 1)\tilde{v}^{-4/3} \tag{2}$$

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(20) Excess volumes for several polymer–solvent systems have been summarized in Table I, P. J. Flory, *Discuss. Faraday Soc.*, **49**, 7 (1970).

Table I
Relative Excess Volumes

w_{PM}	V^E/V^0 140°	150°	160°	170°
0.281		−0.0092	−0.0102	
0.387	−0.0100	−0.0111	−0.0122	−0.0136
0.445	−0.0102	−0.0113	−0.0125	−0.0140
0.557	−0.0104	−0.0115	−0.0126	−0.0140
0.594	−0.0099	−0.0109	−0.0120	−0.0135
0.617	−0.0101	−0.0112		
0.764	−0.0071	−0.0079	−0.0086	−0.0097

Table II
Excess Coefficients of Thermal Expansion

w_{PM}	$\alpha^E \times 10^4$ (deg^{-1}) 140°	150°	160°	170°
0.281		−1.1	−1.2	
0.387	−1.1	−1.2	−1.4	−1.6
0.445	−1.1	−1.3	−1.5	−1.7
0.557	−1.1	−1.3	−1.5	−1.6
0.594	−1.0	−1.2	−1.4	−1.6
0.617	−1.1	−1.2		
0.764	−0.7	−0.9	−1.1	−1.3

The reduced volume $\tilde{v}$ of the solution is related to its specific volume through the equation

$$\tilde{v} = v_{\mathrm{sp}}/v_{\mathrm{sp}}^* \tag{3}$$

where the reducing parameter v_{sp}^* depends on the specific volume and thermal expansion coefficient

$$\alpha_i = \frac{1}{v_{\mathrm{sp};i}}\left(\frac{\partial v_{\mathrm{sp};i}}{\partial T}\right)_p$$

of each component.

$$v_{\mathrm{sp}}^* = w_{10}v_{\mathrm{sp};10}^* + w_{\mathrm{PM}}v_{\mathrm{sp;PM}}^* \tag{4}$$

$$v_{\mathrm{sp};i}^* = v_{\mathrm{sp};i}\left[\frac{3(1 + \alpha_i T)}{4(1 + \alpha_i T) - 1}\right]^3 \tag{5}$$

Here w_{10} and $w_{\mathrm{PM}} = 1 - w_{10}$ are the weight fractions of the two components.

The reduced temperature for the solution is

$$\tilde{T} = \frac{T}{T^*} = \frac{\phi_{10}p_{10}^*\tilde{T}_{10} + \phi_{\mathrm{PM}}p_{\mathrm{PM}}^*\tilde{T}_{\mathrm{PM}}}{\phi_{10}p_{10}^* + \phi_{\mathrm{PM}}p_{\mathrm{PM}} - \phi_{10}\theta_{\mathrm{PM}}X_{12}} \tag{6}$$

The characteristic pressure p_i^*, reduced temperature $\tilde{T}_i$, segment fraction ϕ_i, and surface fraction θ_i for component i can be obtained from the following expressions

$$p_i^* = \gamma_i T\tilde{v}_i^2 \tag{7}$$

$$\gamma_i = \left(\frac{\partial p}{\partial T}\right)_{v_{\mathrm{sp};i}} \tag{8}$$

$$\tilde{v}_i = \frac{v_{\mathrm{sp};i}}{v_{\mathrm{sp};i}^*} \tag{9}$$

$$\tilde{T}_i = (\tilde{v}_i^{1/3} - 1)/v_i^{4/3} \tag{10}$$

$$\phi_i = w_i v_{\mathrm{sp};i}^*/(w_{10}v_{\mathrm{sp};10}^* + w_{\mathrm{PM}}v_{\mathrm{sp;PM}}^*) \tag{11}$$

$$\theta_i = \phi_i s_i/(\phi_{10}s_{10} + \phi_{\mathrm{PM}}s_{\mathrm{PM}}) \tag{12}$$

The parameter s_i is a count of the interaction sites per segment (*cf.* below) of component i. The quantity X_{12} in eq 6 is an interaction parameter peculiar to the component pair.

In the application of this model to mixtures of normal alkanes, it was found convenient to treat each molecule as a linear chain of $r = n + 1$ segments, where n represents the number of carbon atoms in the molecule.[21] The total number of interaction sites per molecule is expressed as

Table III
Properties at 150° for n-Decane and Polymethylene[a]

$v_{\mathrm{sp};10} = 1.5974 \pm 0.0005$ cm^3 g^{-1}	$v_{\mathrm{sp;PM}} = 1.2853 \pm 0.0010$ cm^3 g^{-1}
$\alpha_{10} = (1.429 \pm 0.007) \times 10^{-3}$ deg^{-1}	$\alpha_{\mathrm{PM}} = (0.722 \pm 0.003) \times 10^{-3}$ deg^{-1}
$\tilde{v}_{10} = 1.4261$	$\tilde{v}_{\mathrm{PM}} = 1.2528$
$\tilde{T}_{10} = 0.07825$	$\tilde{T}_{\mathrm{PM}} = 0.05778$
$p_{10}^* = 90.5$ cal deg^{-1}	$p_{\mathrm{PM}}^* = 109.0$ cal deg^{-1}

[a] See ref 21.

$$r_i s_i = r_i s_{\mathrm{m}} + s_{\mathrm{e}} \tag{13}$$

The number of contacts for a midchain segment is s_{m}; s_{e} corrects for the excess sites associated with the chain ends. Only the ratio $s_{\mathrm{e}}/s_{\mathrm{m}}$ is needed for the calculation of θ_i in eq 12.

The relative excess volumes of mixing have been calculated from the expression

$$\frac{V^E}{V^0} = \frac{\tilde{v} - \phi_{10}\tilde{v}_{10} - \phi_{\mathrm{PM}}\tilde{v}_{\mathrm{PM}}}{\phi_{10}\tilde{v}_{10} + \phi_{\mathrm{PM}}\tilde{v}_{\mathrm{PM}}} \tag{14}$$

Excess coefficients of thermal expansion can be computed from the theory using the equation

$$\alpha^E = \alpha - \phi_{10}\frac{\tilde{v}_{10}}{\tilde{v}}\alpha_{10} - \phi_{\mathrm{PM}}\frac{\tilde{v}_{\mathrm{PM}}}{\tilde{v}}\alpha_{\mathrm{PM}} \tag{15}$$

Comparison with Experiment. The values of parameters that are required for computing V^E and α^E at 150° are listed in Table III. Except for p_{10}^*, they have been determined directly from measured values[21] of the density, thermal expansion coefficient, and thermal pressure coefficient γ_i of the two components at 150° according to the prescription in the preceding section. The parameters for polymethylene were obtained from data for Marlex 50 for which r_{PM} has been taken to be 660.[21] The characteristic pressure of decane p_{10}^* was calculated by interpolating values of p^* with chainlength.[21]

The quantities $s_{\mathrm{e}}/s_{\mathrm{m}} = 0.6$ and $X_{12} = 1.16$ have values identical with those used earlier in a study of binary mixtures of n-alkanes.[13,21] Calculated values of V^E/V^0 and α^E are insensitive to their precise values.

Relative excess volumes, calculated for 150° from eq 14, are shown as a solid line in Figure 1. They are in good agreement with those obtained from experiment. The discrepancies between theoretical and experimental values found here (7–15% of the measured V^E/V^0) are comparable, both in magnitude and sign, with those reported[13] for a number of binary mixtures of n-alkanes.

Excess coefficients of thermal expansion for these solutions have been calculated from eq 15. The thermal expansion coefficient of the solution required for this calculation has been found using the formula

$$\alpha T = \frac{3(\tilde{v}^{1/3} - 1)}{1 - 3(\tilde{v}^{1/3} - 1)} \tag{16}$$

where $\tilde{v}$ is obtained from eq 3 and 4, after substitution of experimental values for α_{10} and α_{PM} in eq 5. The calculated and measured excess expansions at 150° are plotted in Figure 2 as a function of the weight fraction. Their agreement is excellent.

Both V^E/V^0 and α^E offer a good test of the theory in that the calculated values are insensitive to errors in the

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[21] R. A. Orwoll and P. J. Flory, *J. Amer. Chem. Soc.*, 89, 6814 (1967).

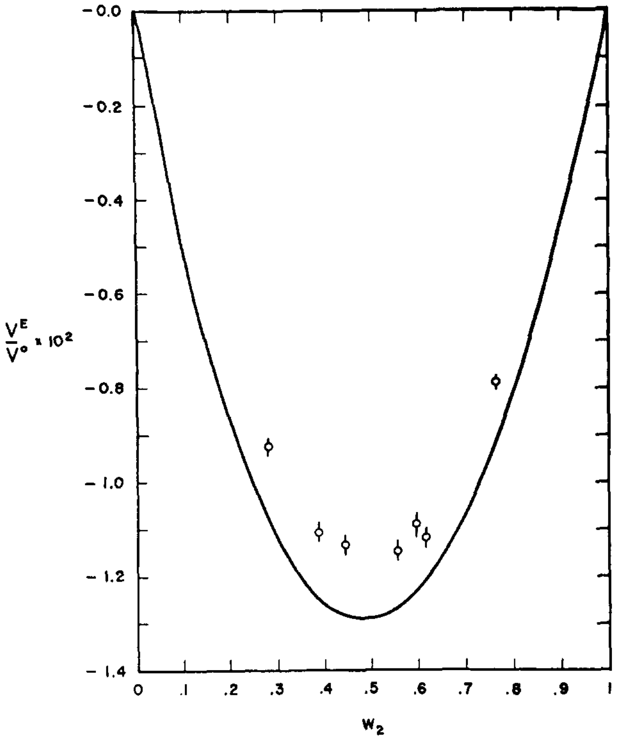

Figure 1. The relative excess volume at 150° for polymethylene in n-decane as a function of the weight fraction of polymethylene. The line has been drawn using eq 14.

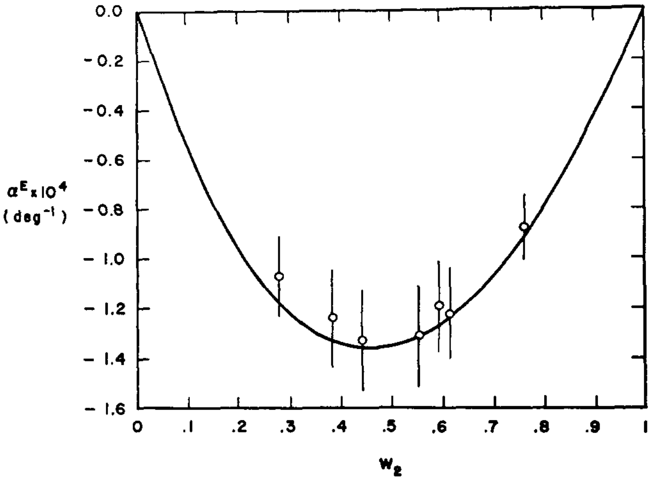

Figure 2. The excess coefficient of thermal expansion at 150° for polymethylene in n-decane as a function of the weight fraction of polymethylene. The line has been drawn according to eq 15.

equation-of-state data of the pure components. For example, for a 50 wt% solution at 150° a 1% error in α_{10} effects a 2% error in V^E/V^0 and only a 3% error in α^E. Under the same conditions, a 1% error in p_{10}^* introduces errors of 2 and 1.5% in V^E/V^0 and α^E, respectively. Large discrepancies between theory and experiment must be attributed to inadequacies in the model.

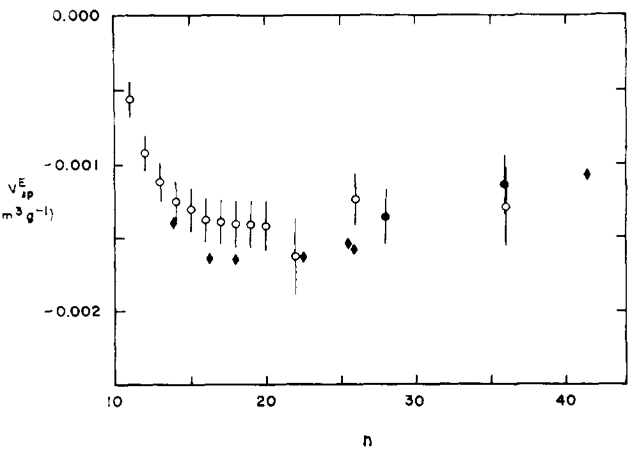

Figure 3. Excess specific volumes of polymethylene and n-decane, shown as diamonds, plotted against the mean chain length n. Superimposed on the plot are the differences $v_{sp;n} - [w_{10}v_{sp;10} + w_{PM}v_{sp;PM}]$ for various pure alkanes. The open circles represent points for which $v_{sp;n}$ were obtained from tabulations in ref 21; the filled circles were calculated from $v_{sp;n}$ from ref 22.

Principle of Congruence. According to Brønsted's principle of congruence[5,17] the specific volume of an alkane of n carbon atoms ($n > 10$) has the same volume as the congruent mixture of decane and polymethylene (*i.e.*, the mixture whose concentration is such that its number-average chain length is n). The weight fraction of polymer in a solution congruent to an alkane of n carbon atoms is given by the equation

$$w_{PM} = \frac{(n - n_{10})M_{PM}}{(n_{PM} - n)M_{10} + (n - n_{10})M_{PM}} \tag{17}$$

where M_{10} and M_{PM} are the molecular weights and n_{10} and n_{PM} are the chain lengths of the components, the latter being taken to be 1000 for these calculations.

The difference between the specific volumes[21,22] of several n-alkanes at 150° and the quantity $(1 - w_{PM})v_{sp;10} + w_{PM}v_{sp;PM}$ is plotted as a function of n in Figure 3. The rather large error bars represent the combined effect of the uncertainties in $v_{sp;10}$, $v_{sp;n}$, $v_{sp;PM}$, and M_{PM}.

The measured excess specific volumes have been located on the same graph. They consistently lie below the locus of points determined by the pure alkanes. This is just the reverse of observations[5,6,9] reported for mixtures of low molecular weight homologs; *i.e.*, in the latter instance the measured excess volumes were found *above* the volumes calculated from data for pure alkanes. This represents additional evidence for small discrepancies in the principle of congruence.[12]

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