CONCENTRATION AND TEMPERATURE DEPENDENCE ON THE PARTIAL
SPECIFIC VOLUME OF POLYSTYRENE IN TETRALIN

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ABSTRACT

In the previous communications we have used the value of the partial specific volume, \( v_2 \), of polystyrene, PS, derived by Höcker et al (1) for determining the molecular weight of the polymer by light scattering (2), viscosity slope constant (3,4) and the excluded volume parameter (5,6).

The partial specific volume is a characteristic parameter of the polymer. This parameter depends on both intra- and intermolecular segment-segment interactions. Hence, several reports (7-11) considered the dependence of \( v_2 \) on the solvent, concentration and temperature.

Hence, specific volume measurements on solutions of PS sample in tetralin, Tet., at different temperatures and mass fractions were performed.

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Experimental

Materials
The PS used was a sample designated as PS, ($\bar{M} = 3.4 \times 10^5$ g.mol$^{-1}$), which was prepared and provided by R.A.P.R.A', Shawbury, Shrewsbury, England (Courtesy Mr. L.J. Maisey). Tet. was dried over sodium wire and distilled twice at atmos. pressure.

Density Measurements
The densities of pure Tet. and Tet./PS solutions were measured at different temperatures dilatometrically. The dilatometers had been calibrated with mercury (12) to determine their volumes up to a fixed mark and capillary radii.

Five concentrations of PS3 solutions in the range of 0.023 to 0.059 kg dm$^{-3}$ were prepared, in each case, gravimetrically. The densities were determined at different temperatures in the range of 293.15 - 343.15 K.

Results and Discussion

The partial specific volume of the solute, $\bar{v}_2$, can be evaluated if the specific volume of the solution, $V$, is known as a function of the composition, $w_2$. If the dependence of $V$ on $w_2$ can be written as

$$V = V_{10} + A_1 w_2 + A_2 w_2^2$$

where $V_{10}$ is the specific volume of the solvent and $A_1$ and $A_2$ are co-efficients to be determined.

The densities $\rho$ of pure Tet. and PS solutions in Tet. at different temperatures are listed in table 1.

The relation of $\rho$ to temperature $T$ at the particular PS concentration is linear, see Fig.1. Values of $\rho$ at 371.15 K were obtained by extra polation of straight lines to this temperature.

The specific volumes of the pure solvent and the solutions were obtained from the densities. The co-efficients $A_1$ and $A_2$ were obtained by fitting the specific volumes, at each temperature, to a quadratic equation. These values are listed in table 2. The expression (13)

$$\bar{v}_2 = V + (1 - w_2) \frac{dV}{dw_2}$$

reveals that the partial specific volume of the solute can be evaluated from eq. 1 since

$$\bar{v}_2 = V_{10} + A_1 + 2 A_2 w_2 - A_2 w_2^2$$

Here

$$V_{10} + A_1 = (\bar{v}_2) w_2 = 0$$
where

\[
\bar{v}_2 \neq 0
\]

is the partial specific volume of PS at infinite dilution.

The values of \((\bar{v}_2)_{w=0}\) calculated from eq. 4 are tabulated in table 2. As well as the values of the partial specific volume of PS, \((\bar{v}_2)\).

As is evident from Fig. 3 there is a small but significant concentration dependence of the partial specific volume of PS in Tet. This dependence is more pronounced at higher temperature. A concentration dependence of the partial specific volume has also been reported for PS in toluene and cyclohexane (10) and in trans-decalin (14). There are also report (15) where no concentration dependence has been observed. However, in the present study the partial specific volume of PS in the solution decreases slightly with increasing \(w_2\).

This behaviour agrees with that found in the system PS/trans-decalin (14) whereas a contrary tendency was found for the system PS/toluene and PS/cyclohexane (10). It is rather interesting to mention that the refractive index increment for PS in Tet also shows a concentration dependence (16). Since the partial specific volume and the refractive index increment are quantities which are closely related (17-21).

Fig. 3 shows that the partial specific volume of PS in tetralin, \((\bar{v}_2)_{w=0}\), increases with increasing temperature.

The temperature dependence of partial specific volume of PS is illustrated in Fig. 4. The variation of \((\bar{V}_2)\) as a function of \(T\) obtained by least squares analysis is given by eq. 5

\[
\bar{v}_2 \neq 1 = 0.9194 + 5.521 \times 10^{-4}(T - 273.15)
\]

The temperature dependence, \((d\bar{v}_2/ dt)_{w=1}\), obtained from the slope of the straight line was found to be \(5.521 \times 10^{-4}\). This value in good accord with the value of \(5.52 \times 10^{-4}\) obtained by Höcker et al (1).

REFERENCES

TABLE (1)

Densities of tet. and PS solutions in Tet. at different temperatures

<table>
<thead>
<tr>
<th>Solution</th>
<th>$w_2$</th>
<th>303.15</th>
<th>313.15</th>
<th>323.15</th>
<th>333.15</th>
<th>343.15</th>
<th>371.15*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tet</td>
<td>0</td>
<td>0.96349</td>
<td>0.95599</td>
<td>0.94849</td>
<td>0.94099</td>
<td>0.93349</td>
<td>0.9122</td>
</tr>
<tr>
<td>A</td>
<td>0.02341</td>
<td>0.96528</td>
<td>0.95764</td>
<td>0.9500</td>
<td>0.94236</td>
<td>0.93472</td>
<td>0.9130</td>
</tr>
<tr>
<td>B</td>
<td>0.0306</td>
<td>0.96589</td>
<td>0.95823</td>
<td>0.95057</td>
<td>0.9429</td>
<td>0.93524</td>
<td>0.91349</td>
</tr>
<tr>
<td>C</td>
<td>0.0397</td>
<td>0.96686</td>
<td>0.95913</td>
<td>0.95141</td>
<td>0.94368</td>
<td>0.93595</td>
<td>0.9140</td>
</tr>
<tr>
<td>D</td>
<td>0.0497</td>
<td>0.96792</td>
<td>0.96015</td>
<td>0.95238</td>
<td>0.94462</td>
<td>0.93685</td>
<td>0.9148</td>
</tr>
<tr>
<td>E</td>
<td>0.0591</td>
<td>0.96900</td>
<td>0.96118</td>
<td>0.95336</td>
<td>0.94553</td>
<td>0.93771</td>
<td>0.91550</td>
</tr>
</tbody>
</table>

Coefficients of least squares fitting

\[
\begin{align*}
a & \approx 0.986 \\
\frac{-b \times 10^4}{\text{kg} \cdot \text{dm}^{-3} \text{deg}^{-1}} & \approx 7.502
\end{align*}
\]

\[
\begin{align*}
a & \approx 0.988 \\
\frac{-b \times 10^4}{\text{kg} \cdot \text{dm}^{-3} \text{deg}^{-1}} & \approx 7.64
\end{align*}
\]

\[
\begin{align*}
a & \approx 0.989 \\
\frac{-b \times 10^4}{\text{kg} \cdot \text{dm}^{-3} \text{deg}^{-1}} & \approx 7.661
\end{align*}
\]

\[
\begin{align*}
a & \approx 0.990 \\
\frac{-b \times 10^4}{\text{kg} \cdot \text{dm}^{-3} \text{deg}^{-1}} & \approx 7.729
\end{align*}
\]

\[
\begin{align*}
a & \approx 0.991 \\
\frac{-b \times 10^4}{\text{kg} \cdot \text{dm}^{-3} \text{deg}^{-1}} & \approx 7.766
\end{align*}
\]

\[
\begin{align*}
a & \approx 0.992 \\
\frac{-b \times 10^4}{\text{kg} \cdot \text{dm}^{-3} \text{deg}^{-1}} & \approx 7.822
\end{align*}
\]

Where the least squares fitting is in accord with

\[
\rho = a + b (T - 273.15)
\]

* Values of density at 371.15 were obtained by extrapolation of the straight lines to this temperature.
### TABLE (2)

Results from Specific Volume Measurements on the System PS/Tet.

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>$V_{10}$ (dm$^3$/kg)</th>
<th>$-\Lambda_1$ (dm$^3$/kg)</th>
<th>$-\Lambda_2$ (dm$^3$/kg)</th>
<th>$(\frac{\bar{v}<em>2}{w_2})</em>{w_2=0}$ (dm$^3$/kg)</th>
<th>$-(\frac{d\bar{v}<em>2}{dw_2})</em>{w_2=0}$ (dm$^3$/kg)</th>
<th>$\bar{v}_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>293.15</td>
<td>1.03011</td>
<td>0.10411</td>
<td>0.00475</td>
<td>0.92600</td>
<td>0.0095</td>
<td>0.93075</td>
</tr>
<tr>
<td>303.15</td>
<td>1.03813</td>
<td>0.09969</td>
<td>0.0024</td>
<td>0.93844</td>
<td>0.0048</td>
<td>0.93604</td>
</tr>
<tr>
<td>313.15</td>
<td>1.04627</td>
<td>0.09477</td>
<td>0.01008</td>
<td>0.9515</td>
<td>0.02016</td>
<td>0.94142</td>
</tr>
<tr>
<td>323.15</td>
<td>1.05455</td>
<td>0.09047</td>
<td>0.01724</td>
<td>0.96408</td>
<td>0.03448</td>
<td>0.94684</td>
</tr>
<tr>
<td>333.15</td>
<td>1.06295</td>
<td>0.08494</td>
<td>0.02572</td>
<td>0.97801</td>
<td>0.05144</td>
<td>0.95229</td>
</tr>
<tr>
<td>343.15</td>
<td>1.07149</td>
<td>0.08004</td>
<td>0.03369</td>
<td>0.99145</td>
<td>0.06738</td>
<td>0.95776</td>
</tr>
<tr>
<td>371.15</td>
<td>1.09634</td>
<td>0.05587</td>
<td>0.06637</td>
<td>1.04047</td>
<td>0.13274</td>
<td>0.9741</td>
</tr>
</tbody>
</table>
Fig. 1 Dependence of the density of PS solutions (A-E) on weight fraction of PS, $w_2$, at different temperatures, $T$ (K). Designation of solutions, as in Table 1.
Fig. 2 Variation of partial specific volume of PS in Tet, 
$(\bar{\nu}_2)_{w_2=0}$ at different temperatures with weight fraction of PS, $w_2$. 
Fig. 4 Dependence of Partial Specific Volume of PS, \( \bar{v}_2 \), on Temperature.