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, $\bar{v}_2$, 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 inter molecular segment-segment interactions. Hence, several reports (7-11) considered the dependence of $\bar{v}_2$ 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_3 ($\overline{M}_w = 3.4 \times 10^5$ 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, $\overline{v}_2$, 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

$$V = V_{10} + A_1 w_2 + A_2 w_2^2 \qquad\qquad (1)$$

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

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

The relation of ρ to temperature T at the particular PS concentra-
tion is linear, see Fig.1. Values of ρ 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)

$$\overline{v}_2 = V + (1 - w_2) \frac{dV}{dw_2} \qquad\qquad (2)$$

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

$$\overline{v}_2 = V_{10} + A_1 + 2 A_2 w_2 - A_2 w_2^2 \qquad\qquad (3)$$

Here

$$V_{10} + A_1 = (\overline{v}_2)_{w_2 = 0} \qquad\qquad (4)$$

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where

$(\bar{v}_2)_{w_2= 0}$ is the partial specific volume of PS at infinite dilution.
The values of $(\bar{v}_2)_{w_2= 0}$ 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 depend-
ence 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 in good agreement 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 closly re-
lated (17-21).

Fig. 3 shows that the partial specific volume of PS in tetralin, $(\bar{v}_2)_{w_2= 0}$,
increases with increasing temperature.

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

$$(\bar{v}_2)_{w_2= 1} = 0.9194 + 5.521 \times 10^{-4}(T - 273.15) \tag{5}$$

The temperature dependence, $(d\bar{v}_2/ dt)_{w2= 1}$, obtained from the slope
of the straight line was found to be 5.521×10^{-4}. This value in
a good accord with the value of 5.52×10^{-4} obtained by Höcker et al(1)
for PS.

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TABLE (1)

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

Solution		Density (Kg dm^{-3}) at temperatures T°						Coefficients of least squares fitting		
designation	w_2	303.15	313.15	323.15	333.15	343.15	371.15*	$\frac{a}{kg. dm^{-3}}$	$-b \times 10^4$ $kg. dm^{-3} deg^{-1}$	
Tet	0	0.96349	0.95599	0.94849	0.94099	0.93349	0.9122	0.986	7.502	
A	0.02341	0.96528	0.95764	0.9500	0.94236	0.93472	0.9130	0.988	7.64	
B	0.0306	0.96589	0.95823	0.95057	0.9429	0.93524	0.91349	0.989	7.661	
C	0.0397	0.96686	0.95913	0.95141	0.94368	0.93595	0.9140	0.990	7.729	
D	0.0497	0.96792	0.96015	0.95238	0.94462	0.93685	0.9148	0.991	7.766	
E	0.0591	0.96900	0.96118	0.95336	0.94553	0.93771	0.91550	0.992	7.822	

Where the least squares fitting is in accord with

$$= a + b (T - 273.15)$$

* Values of density at 371.55 were obtained by extrapolation of the straight lines to this temperature.

TABLE (2)

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

Temp. (K)	V_{10} (dm^3/kg)	$-A_1$ (dm^3/kg)	$-A_2$ (dm^3/kg)	$(\bar{v}_2)_{w2=0}$ (dm^3/kg)	$-(d\bar{v}_2/dw_2)_{w2=0}$ (dm^3/kg)	$(\bar{v}_2)$
293.15	1.03011	0.10411	0.00475	0.92600	0.0095	0.93075
303.15	1.03813	0.09969	0.0024	0.93844	0.0048	0.93604
313.15	1.04627	0.09477	0.01008	0.9515	0.02016	0.94142
323.15	1.05455	0.09047	0.01724	0.96408	0.03448	0.94684
333.15	1.06295	0.08494	0.02572	0.97801	0.05144	0.95229
343.15	1.07149	0.08004	0.03369	0.99145	0.06738	0.95776
371.15	1.09634	0.05587	0.06637	1.04047	0.13274	0.9741

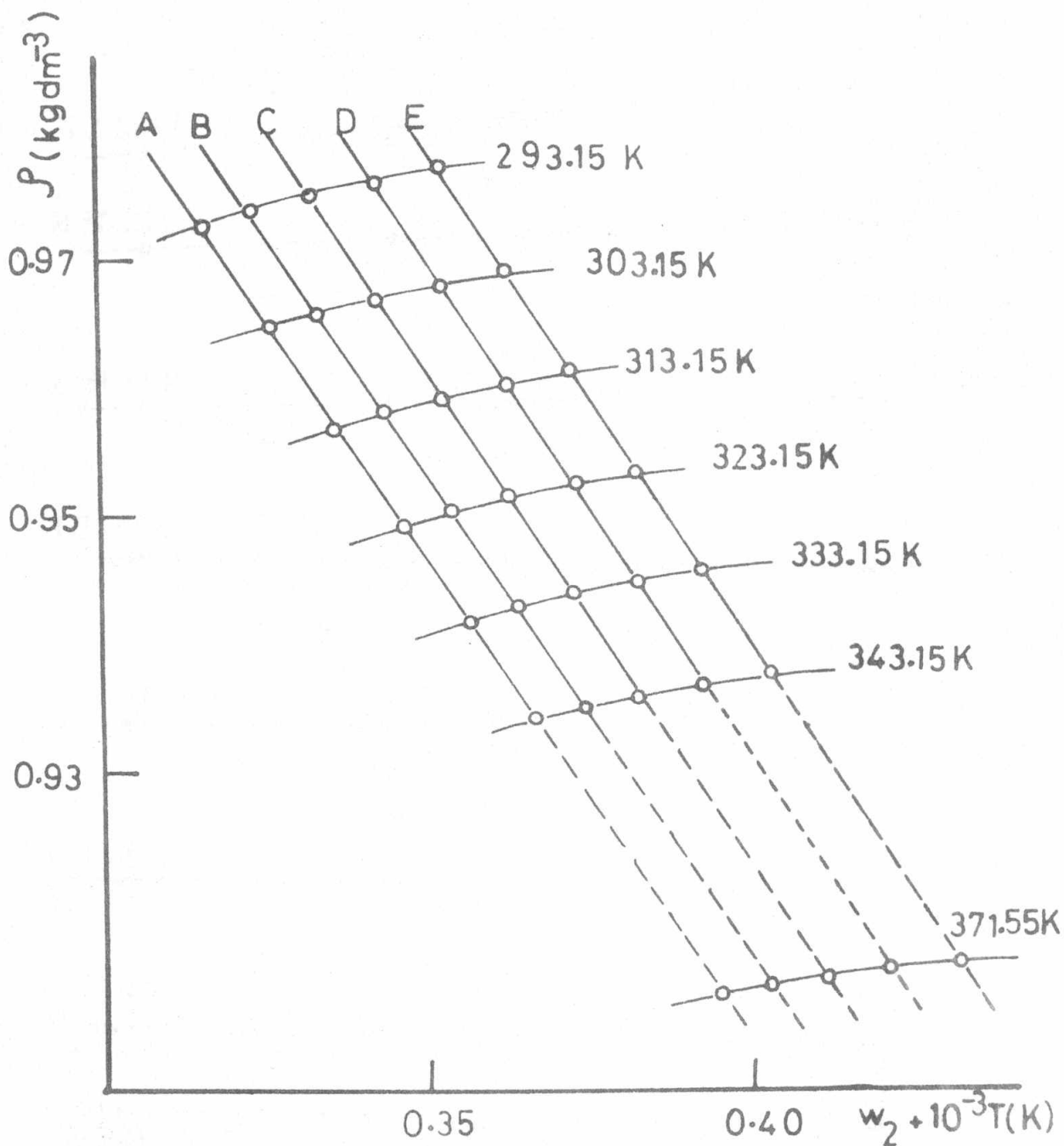Fig. 1   Dependence of the density of PS solutions (A-E) on weight fraction of PS, W_2, at different temperatures, T (K). Designation of solutions, as in Table 1.
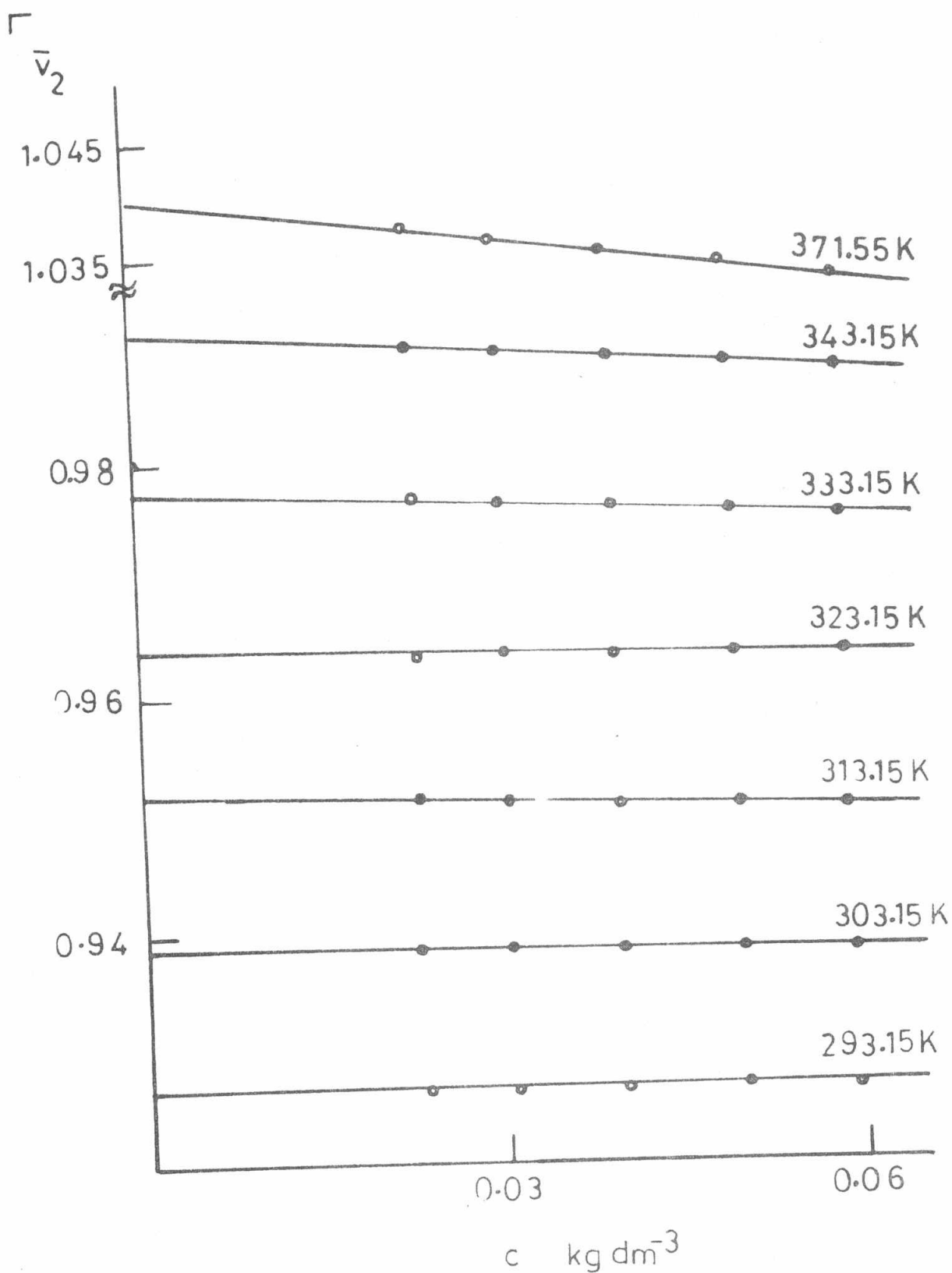
Fig. 2 Variation of partial specific volume of PS in Tet,
$(\bar{v}_2)_{w_2 = 0}$ at different temperatures with weight
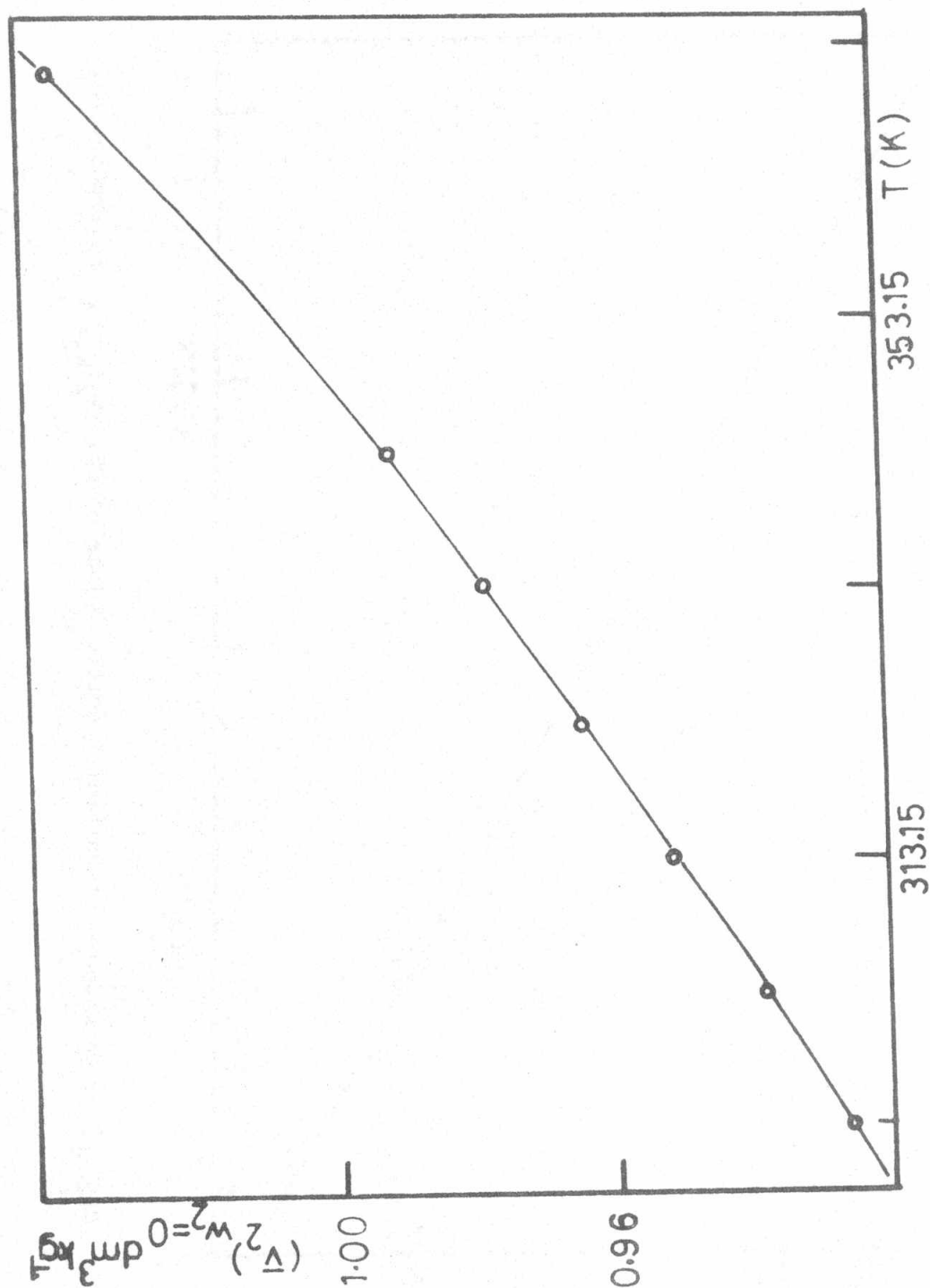fraction of PS, w_2.

Fig. 3   Variation of partial specific volume of PS in Tet, $(\bar{v}_2)_{w_2 = 0}$, with temperature.
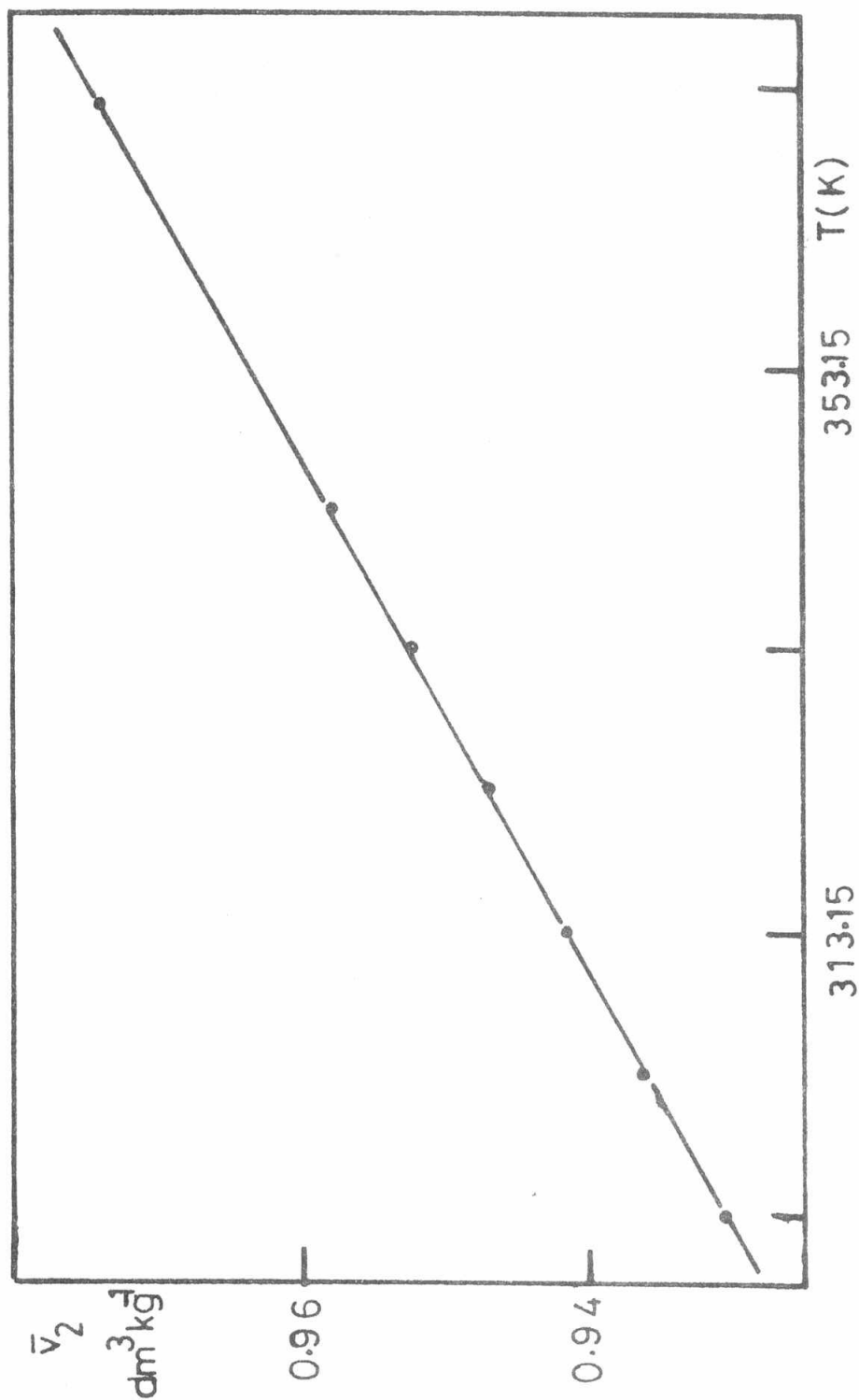
Fig. 4   Dependence of Partial Specific Volume of PS, $(\bar{v}_2)_{w_2 = 1}$ on Temperature.