

Sedimentation velocity measurements close to the upper critical solution temperature and at θ -conditions: polystyrene in cyclopentane over a large concentration interval

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(Received 5 September 1978)

Sedimentation velocity measurements on polystyrene ($M = 110\,000$) in cyclopentane over an extended concentration region and from 5°C (close to the upper critical solution temperature) to 40°C are reported. The concentration dependence parameter $(k_s)_w$ increases from 2 to 5°C to 27 at 40°C . For all temperatures except 5°C , s_0/s vs. $w[\eta]_w$ shows an upward curvature at $w[\eta]_w \approx 1$; at 5°C , on the other hand, s_0/s is independent of concentration over the region considered. Furthermore, measurements have also been performed at 20°C (θ -conditions) over a large concentration interval for the molecular weights $M = 20\,400$, $390\,000$ and $950\,000$. The parameters s_0 and $(k_s)_w$ were both found to be proportional to $\bar{M}_w^{1/2}$. In the 'hydrodynamically normalized' plot s_0/s vs. $w[\eta]_w$ the sedimentation behaviour can approximately be represented by a single curve for all the molecular weights.

INTRODUCTION

Transport phenomena in concentrated macromolecular solutions have been investigated quite extensively during the past few years¹⁻¹¹. In particular sedimentation velocity measurements over a large concentration interval have been of great interest¹¹⁻²⁰. Recently, the sedimentation process in a polymer-solvent system (polystyrene/*trans*-decalin), where θ -conditions could be altered to good solvent conditions by an increase in temperature, was studied both in dilute and concentrated solutions¹⁶. It was observed that in dilute solution the empirical concentration dependence parameter, k_s , was positive at the θ -temperature and increased with increasing temperature, in agreement with measurements on other systems^{15,18,21-24}. Furthermore, when the concentration was increased, the sedimentation behaviour at θ -conditions changed markedly at $c[\eta] \approx 1$ (c is the concentration in mass per unit volume and $[\eta]$ is the limiting viscosity number) and approached that at good solvent conditions at still higher concentrations.

The complexity of the sedimentation behaviour in concentrated macromolecular solutions, especially near phase separation, was demonstrated from measurements on polystyrene in cyclohexane close to the upper critical solution temperature (UCST) where no dependence of the sedimentation coefficient on concentration was found¹⁸. In order to further elucidate the sedimentation process at the θ -temperature, and also to study the behaviour close to the UCST the present investigation on another polymer-solvent system with an ambient θ -temperature was undertaken. Sedimentation velocity measurements at the θ -temperature were performed in cyclopentane on polystyrene samples with

various molecular weights (see *Table 1*) and at solute mass fractions ranging from 0.002 to 0.22. The θ -temperature for the present system is reported to be 20°C ²⁵. For the polystyrene sample with $M = 110\,000$ measurements were also carried out at temperatures ranging from 5° to 40°C . From data in the literature²⁶, the UCST for this sample was determined to be 3.8°C .

EXPERIMENTAL

Sample, solvent and preparation of solutions

Polystyrene samples with narrow molecular weight distribution, from Pressure Chemical Co., Pittsburgh, Pa, were used as received. The nominal molecular weights, according to the manufacturer's specification, and characteristic data for the samples are given in *Table 1*.

Spectroscopic grade cyclopentane (Merck) was used without further purification in all measurements. All solutions were prepared by weighing; after addition of solvent the polymer was allowed to swell before the solution was homogenized by stirring for several days. The composition of the solutions is expressed in weight fraction, w , of the solute.

Table 1 Characteristic data for the polystyrene samples

Lot No.	Nominal molecular weight (M)	\bar{M}_w (kg/mol)	$\frac{\bar{M}_w}{\bar{M}_n}$
2b	20 400	20.8	<1.06
4b	110 000	111	<1.06
3b	390 000	392	<1.10
61208	950 000	900	<1.10

Table 2 Sedimentation velocity results for polystyrene ($M = 110\,000$) in cyclopentane at various temperatures

$w \times 10^2$	$s \times 10^{13}/(\text{sec})$					
	5°C	11°C	15°C	20°C	30°C	40°C
0	8.07 ^a	8.40 ^a	8.84 ^a	8.90 ^a	9.94 ^a	11.03 ^a
0.278	8.07	—	—	—	—	—
0.280	—	8.00	8.50	8.34	9.35	10.12
0.538	7.82	—	—	—	—	—
0.559	—	7.89	8.08	8.00	8.76	9.49
0.822	7.98	7.73	7.83	7.88	8.43	9.06
1.02	—	7.70	7.62	7.69	7.99	8.86
1.03	7.89	—	—	—	—	—
1.25	8.02	7.58	7.30	7.41	7.82	8.24
1.91	7.79	6.85	6.77	6.85	6.89	7.17
2.68	7.62	6.49	—	5.99	—	6.40
4.86	7.75	5.25	—	4.38	—	4.45
7.46	7.69	3.82	—	2.97	—	3.04
9.80	7.68	2.57	—	2.05	—	2.20
12.2	7.73	1.75	—	1.52	—	1.65
16.8	7.71	1.02	—	0.95	—	1.08

^a Obtained by extrapolation to $w = 0$ in a plot of $1/s$ vs. w (see the main text). The s values are calculated according to Method I in reference 28 and correspond to a certain average pressure which is the same in all measurements

Table 3 Sedimentation velocity results for polystyrene in cyclopentane at the θ -temperature (20°C)

$M = 20\,400$		$M = 390\,000$		$M = 950\,000$	
$w \times 10^2$	$s \times 10^{13}$ (sec)	$w \times 10^2$	$s \times 10^{13}$ (sec)	$w \times 10^2$	$s \times 10^{13}$ (sec)
0	3.97 ^a	0	16.12 ^a	0	26.60 ^a
0.6433	3.68	0.2109	14.56	0.2404	23.04
1.506	3.52	0.4191	14.21	0.5322	20.11
1.905	3.42	0.6630	13.14	0.8780	16.56
2.483	3.14	0.8575	12.01	1.392	12.33
3.658	2.73	1.117	11.79	1.827	10.27
5.496	2.42	2.404	8.53	2.045	8.97
7.105	2.09	3.851	5.85	2.767	7.03
8.230	1.77	5.521	3.71	4.140	5.03
11.92	1.20	7.489	2.85	5.289	4.00
15.90	0.88	10.90	1.77	6.768	2.99
21.43	0.58	—	—	8.016	2.44

^a Obtained by extrapolation to $w = 0$ in a plot of $1/s$ vs. w (the main text). The s values are calculated according to Method I in reference 28 and correspond to a certain average pressure which is the same in all measurements

Velocity sedimentation

Ultracentrifugation was carried out at 60 000 rpm using an MSE analytical ultracentrifuge (Centriscan 75) equipped with a schlieren optical system of the photoelectric scanning type²⁷, and a temperature controlling unit. The principles of the performance of sedimentation measurements and the evaluation of sedimentation coefficients have been discussed previously²⁸. Sedimentation coefficients were for all samples determined at 20°C (θ -temperature) and for sample 4b ($M = 110\,000$) also at 5, 11, 15, 30 and 40°C, and at solute mass fractions ranging from 0.002 and 0.22. The experimental results are collected in Tables 2 and 3.

Viscometry

Viscosity measurements on sample 4b ($M = 110\,000$) were performed in a viscometer of the Ubbelohde type. The kinetic energy correction and the shear dependence of solution

viscosity were both found negligible. Values of $[\eta]_w$ are listed in Table 4.

RESULTS AND DISCUSSION

Dilute solutions

The equation:

$$\frac{1}{s} = \frac{1}{s_0} [1 + (k_s)_w w] \quad (1)$$

where s and s_0 denote the sedimentation coefficients at solute mass fraction w and at infinite dilution, respectively, is appropriate for the analysis of sedimentation data in dilute solutions. $(k_s)_w$ is a characteristic of the solute-solvent pair considered, and depends on the temperature of measurement and on solute molecular weight [$(k_s)_w \equiv (k_s)_c \rho_0$ where $(k_s)_c$ is the corresponding parameter for concentration, c , in mass per volume and ρ_0 is the density of the solvent]. The values of s_0 and $(k_s)_w$ listed in Tables 2, 3 and 4, respectively, were determined according to equation (1).

The parameter $(k_s)_w$ increases when the temperature is removed from the UCST (see Figure 1). This behaviour is predicted by recent theories^{29,30}. It should be observed that $(k_s)_w$ seems to be close to zero (or even zero) at the UCST; this tendency has also been observed for other polymer-solvent systems^{18,21-23}. The ratio $(k_s)_w/[\eta]_w$, where $[\eta]_w \equiv [\eta]_c \rho_0$, has a similar temperature dependence as $(k_s)_w$ (see Figure 1). This is expected since $[\eta]_w$ varies only slightly over the temperature interval considered (see Table 4). The

Table 4 Quantities for polystyrene in cyclopentane determined from experimental data

M	t (°C)	$(k_s)_w$	$[\eta]_w$	$\frac{(k_s)_w}{[\eta]_w}$
20 400	20.0	9.7	—	—
110 000	5.0	2.0	22	0.09
	11.0	10.9	23	0.47
	15.0	16.1	23	0.65
	20.0	17.1	23	0.74
	30.0	22.9	24	0.95
	40.0	27.0	24	1.12
390 000	20.0	36.5	—	—
950 000	20.0	64.9	—	—

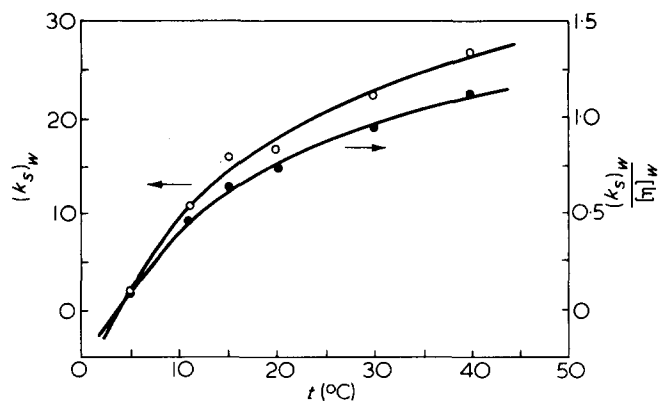


Figure 1 Temperature dependence of $(k_s)_w$ and $(k_s)_w/[\eta]_w$ for polystyrene ($M = 110\,000$) in cyclopentane

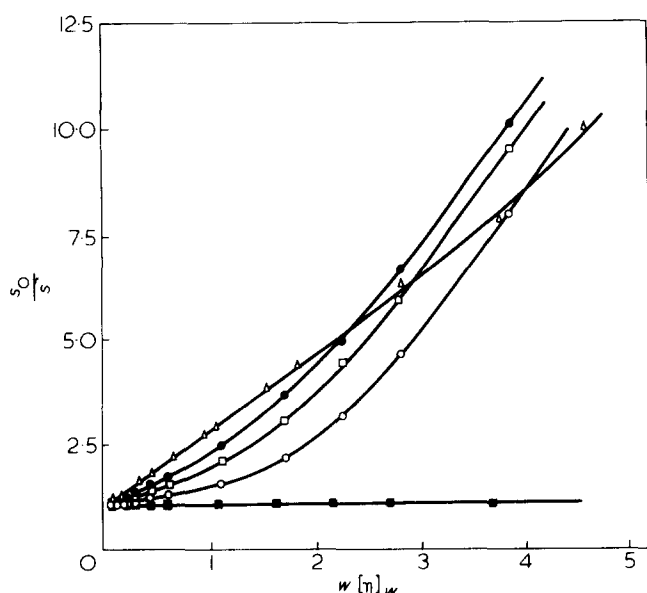


Figure 2 Plot of s_0/s vs $w[\eta]_w$ for polystyrene ($M = 110\,000$) in cyclopentane: ■, 5°C; ○, 11°C; □, 20°C; ●, 40°C, and in toluene: △, 25°C¹¹

value of $(k_s)_w/[\eta]_w$ at the θ -temperature has been predicted by the following theories:

$$\frac{(k_s)_w}{[\eta]_w} \equiv \frac{(k_s)_c}{[\eta]_c} = \begin{cases} 0.2 & \text{(Yamakawa³¹)} \\ 0.6 \pm 0.1 & \text{(Pyun-Fixman³⁰, Billick²¹)} \\ 1 & \text{(Freed³²)} \\ 1 & \text{(Imai³³)} \end{cases}$$

The value 0.77, at the θ -temperature (20°C), obtained from Figure 1, appears to be in the best agreement with the theoretical value of Pyun and Fixman. The same statement has been made for the system polystyrene/*trans*-decalin investigated previously¹⁶. From a number of investigations it appears as if Yamakawa's theory underestimates the $(k_s)_w/[\eta]_w$ value at the θ -temperature, whereas Freed's and Imai's theories overestimate it.

The molecular weight dependence of s_0 and $(k_s)_w$ at the θ -temperature were experimentally found to be given by the following equations:

$$s_0 = 8.7 \times 10^{-14} \bar{M}_w^{0.50} \quad (\text{at } 20^\circ\text{C}) \quad (2)$$

$$(k_s)_w = 1.9 \bar{M}_w^{0.50} \quad (\text{at } 20^\circ\text{C}) \quad (3)$$

These equations are consistent with the theoretically predicted dependencies at the θ -temperature³³.

The proportionality of k_s and s_0 to $M^{1/2}$ at the θ -temperature has been observed for several polymer-solvent systems^{24,34,35}. Since both $(k_s)_w$ and s_0 are, at the θ -temperature, proportional to $\bar{M}_w^{1/2}$ it follows from equation (1) that the slopes in a plot of $1/s$ vs. w should be independent of molecular weight which also was found, within the experimental uncertainty, for the present system. This feature has also been observed for other systems^{24,34,35}.

Concentrated solutions

The concentration and temperature dependence of the sedimentation coefficient, s , is closely related to that of the frictional coefficient, f , through Svedberg's equation³⁶:

$$s = \frac{M(1 - \bar{v}\rho)}{N_A f} \quad (4)$$

where \bar{v} is the partial specific volume of the solute, M the solute molecular weight, and ρ the solution density. Equation (4) combined with the corresponding relation at infinite dilution, $s_0 = M(1 - \bar{v}_0\rho_0)/N_A f_0$, gives:

$$\frac{s_0}{s} = \frac{(1 - \bar{v}_0\rho_0)}{(1 - \bar{v}\rho)} \times \frac{f}{f_0} \quad (5)$$

The relative change, with concentration or temperature, of the frictional coefficient is, according to equation (5), essentially determined by the corresponding change of the ratio s_0/s . A close inspection of Table 2 reveals that close to the UCST the relative increase of the ratio s_0/s is larger the higher the solute mass fraction is and at higher temperatures this increase tends to become almost independent of w .

In a sufficiently dilute macromolecular solution the transport properties are almost entirely governed by the intrinsic properties of the solute molecules, since they can be considered to behave as individual units. An increase in the concentration will eventually lead to a state where the molecules are in more or less permanent contact. Simha *et al.*^{37,38} considered solutions of flexible macromolecules, and estimated for spherical impenetrable coils the concentration corresponding to incipient overlap to be $c^* = [\eta]_c^{-1}$. A general conclusion³⁹ is that c^* is proportional to $[\eta]_c^{-1}$; the actual proportionality constant being dependent upon the model chosen.

The molecules begin to entangle at concentrations above c^* (or $w^* \equiv c^*/\rho_0$, which will be used in the discussion below), and a situation where a uniform local segment density, over the available volume prevails, will eventually be reached. The sedimentation process at concentrations above c^* is discussed in terms of the 'porous plug' model¹² where the sedimentation of the polymer is closely related to the permeability of this 'plug'. This concept has been elaborated in detail elsewhere^{12,40,41}.

In Figure 2 the transport process over the concentration and temperature intervals is depicted. At 5°C (close to the UCST) s_0/s is almost independent of solution composition over the interval studied; this behaviour has also been observed for polystyrene in cyclohexane¹⁸. This may have its origin in enhanced aggregate formation⁴², especially when the concentration increases. The strong local fluctuations in concentration which occur in the neighbourhood of phase separation may be responsible for this feature. Another plausible explanation for this phenomenon can be that the polymer coils 'collapse' in the vicinity of phase separation. This 'collapse' may assume enhanced importance at elevated concentrations, i.e. near the maximum of the phase separation curve. This decrease in coil dimensions may lead to the observed sedimentation behaviour.

An increase in temperature will lead to a totally different behaviour in the sedimentation process (see Figure 2). The curves s_0/s vs. $w[\eta]_w$ show an upward curvature at $w[\eta]_w \approx 1$; this curvature vanishes gradually with increasing temperature, i.e. when the solvent power increases. A similar behaviour has previously been demonstrated for the system polystyrene/*trans*-decalin¹⁶. For the good polymer-solvent system [polystyrene ($M = 110\,000$) in toluene at 25°C] the analogous curve is almost linear over the investigated region¹¹.

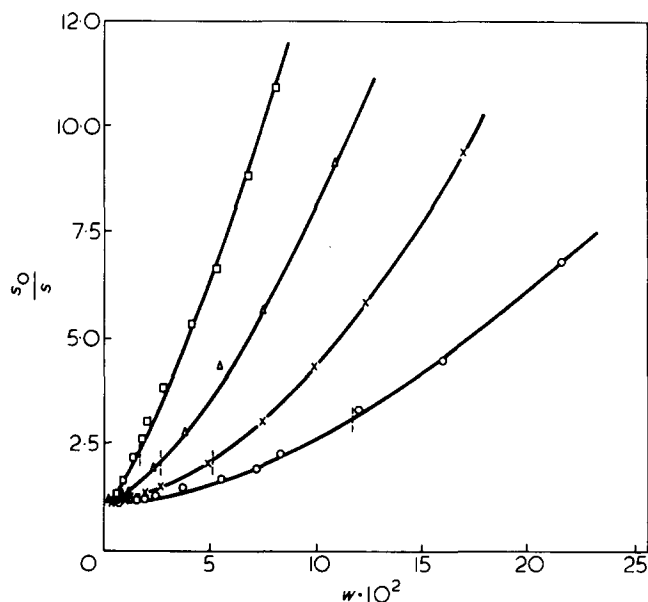


Figure 3 The dependence of s_0/s on solute mass fraction for polystyrene in cyclopentane at the θ -temperature (20°C) (the dashed vertical lines indicate w^*): \circ , $M = 20\,400$; \times , $M = 110\,000$; \triangle , $M = 390\,000$; \square , $M = 950\,000$

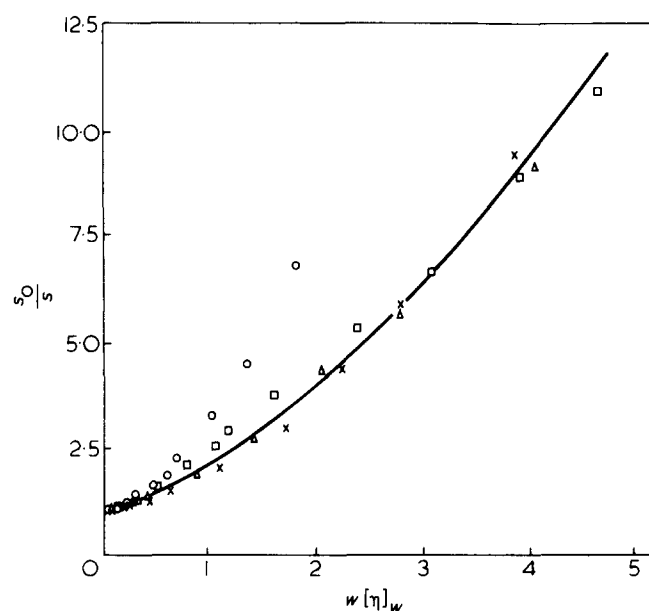


Figure 4 The dependence of s_0/s on $w[\eta]_w$ for polystyrene in cyclopentane at the θ -temperature: \circ , $M = 20\,400$; \times , $M = 110\,000$; \triangle , $M = 390\,000$; \square , $M = 950\,000$

These features can be interpreted by the following arguments. Not too far from θ -conditions the polymer coils can be expected to assume fairly compact conformations. Therefore, the penetration of the coils may be assumed to occur rather abruptly leading to a marked transition from dilute to concentrated solution behaviour as is revealed by the curvatures in Figure 2. On the other hand, when good solvent conditions are approached, the coils become more expanded and the interpenetration of the different coils should be easier and hence the transition is likely to occur smoothly over a relatively large concentration region (Figure 2).

In Figure 3 s_0/s at 20°C (θ -temperature) is plotted vs. w for a number of molecular weights. The basic feature is that the curves become steeper with increasing molecular weight. The upward curvature appears to start approximately at the mass fraction $w^* = [\eta]_w^{-1}$ (indicated by vertical dashed lines), above which the sedimentation process may be described by the permeability concept; values of $[\eta]_w$ were calculated from published data of limiting viscosity numbers²⁵.

The molecular weight dependence of the sedimentation process can be reduced or even eliminated if the sedimentation process can be reduced or even eliminated if the sedimentation data are plotted in a 'hydrodynamically normalized' plot¹³ (see Figure 4). The data can, within the experimental uncertainty, be represented by a single curve for all but the lowest molecular weight. The reason for this discrepancy is at present not clear. However, it should be mentioned that the very small sedimentation coefficients for a low molecular weight sample in highly concentrated solutions may be marred by relatively large errors.

ACKNOWLEDGEMENTS

The authors thank Professors L. -O. Sundelöf and H. Vink for comments concerning the manuscript. This work is part of a research project financially supported by the Swedish Natural Science Research Council.

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