

# Fractional coefficient of macromolecules in concentrated solution and in the vicinity of the critical solution temperature. Diffusion and sedimentation studies of polystyrene in toluene and *trans*-decalin

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The concentration dependence of the frictional coefficient ( $f$ ) in concentrated solutions of well-defined polystyrene fractions has been studied both in a good solvent (toluene) and in a solvent where  $\theta$  conditions and condition in the vicinity of phase separation can be realized (*trans*-decalin).  $f$  and the self-diffusion coefficient ( $D^+$ ) have been calculated from a combination of measured translational diffusion coefficients ( $D$ ) and osmotic pressure data for the systems; polystyrene ( $M = 390\,000$ )/*trans*-decalin up to  $90\text{ kg/m}^3$  at  $20^\circ$  ( $\theta$ -conditions),  $30^\circ$  and  $40^\circ\text{C}$ ; polystyrene ( $M = 110\,000$ )/toluene up to  $120\text{ kg/m}^3$  at  $25^\circ\text{C}$ . Sedimentation measurements are also reported. The main results are: (a) over a concentration interval  $0\text{--}100\text{ kg/m}^3$ ,  $f$  shows more than a ten-fold and almost linear increase; (b) in *trans*-decalin when the temperature is raised from  $20^\circ$  ( $\theta$ -conditions) to  $40^\circ\text{C}$  (good solvent conditions), keeping the concentration constant,  $f$  increases only slightly, the increase being somewhat more pronounced at higher concentrations; (c) the concentration dependence of the ratio  $D/D^+$  is considerable under good solvent conditions but becomes gradually less pronounced when  $\theta$ -conditions are approached; (d) diffusion/osmosis and velocity sedimentation give identical values of  $f$  over the entire concentration interval.

## INTRODUCTION

Diffusion in concentrated macromolecular solutions is a phenomenon which plays an important role in many applications in biology and medicine as well as in technology. A deeper understanding of the process under various conditions is thus very desirable. The rate of diffusion – for a given concentration gradient – depends both on the thermodynamic properties of the system, acting directly in the driving force, and on the way the particle in motion dissipates its energy to the surroundings, usually referred to as the frictional properties of the system. Somewhat oversimplified one may say that the diffusion coefficient can be separated into a thermodynamic and a frictional part or factor (see equations (1) and (5) below). The first factor would then depend on the thermodynamic free energy properties of the system whereas the frictional part would be governed more by the geometry of the particle and the viscosity of the medium. However, the effects cannot be so clearly isolated from each other. The virial coefficients, for instance, appearing in the thermodynamic factor (see equation 5 below) depend to some degree on the geometry of the particle, and *vice versa*, the geometry of the particle, as reflected in the value of the frictional factor (e.g. for chain

polymers) is also determined by the thermodynamic properties of the system. Nevertheless, it is thus clear that in order to obtain a better resolved picture of the diffusion process, measurements of diffusion coefficients should be complemented by thermodynamic measurements of, for example, osmotic pressure, as well as other transport measurements such as sedimentation or self-diffusion.

Over the past few years there has been a fair amount of work, both experimental<sup>1–12</sup> and theoretical<sup>13–18</sup>, on the characterization of the diffusion process in concentrated macromolecular solutions. Although several experimental studies of translational diffusion in concentrated solutions have been carried out, there are few<sup>5,12,19,20</sup> accompanied by osmotic pressure and velocity sedimentation data.

Accurate measurements on macromolecular systems are often hampered by a lack of sufficiently well-defined samples. This lack complicates a detailed study of the diffusion process. In particular, the distribution of molecular weights over a finite interval or the variation in degree of substitution, in the case of a derivative, provides serious difficulties in the interpretation of data. This problem becomes particularly disturbing at higher concentrations, when, for instance, osmotic pressure data are combined with diffusion data, since the type of averages used may influence the re-

sult numerically to a considerable extent as pointed out earlier<sup>8,12</sup>. The present investigation is an attempt to avoid these difficulties by using sharp fractions of polystyrene, which also allow a more precise study of the transport process in the vicinity of phase separation<sup>12</sup> (critical solution temperature). Even if the fractions used in the present work are very sharp there still remains the question of to what extent even a residual width of the molecular weight distribution may affect the higher terms in the virial expansion at elevated concentrations.

This investigation presents results from free diffusion measurements over extended concentration regions (up to about 120 kg/m<sup>3</sup>) for two polystyrene (PS) samples ( $M \approx 110\,000$ , see below) in toluene at 25°C and for one PS sample ( $M \approx 400\,000$ , see below) in *trans*-decalin (t-D) at temperatures ranging from 20° to 40°C allowing in the latter system the thermodynamic properties to be altered from  $\theta$  conditions to good solvent conditions. From osmotic pressure measurements in *trans*-decalin the  $\theta$  temperature is determined to be 20.8°C (vanishing second virial coefficient) and the system is found to approach the good solvent region at 40°C<sup>21</sup>. The diffusion data are combined with osmotic pressure data<sup>21,22</sup> in order to determine the frictional coefficient and its concentration dependence and a comparison is made with velocity sedimentation results<sup>23</sup>.

## THEORY

For a binary system the following expression for the mutual diffusion coefficient,  $D$ , can be derived<sup>14,24</sup> at constant temperature,  $T$ , and pressure,  $P$ :

$$D = \frac{c}{N_A f} \left( \frac{\partial \mu}{\partial c} \right)_{T,P} \quad (1)$$

$\mu$  and  $c$  are the chemical potential and concentration (mass/volume), respectively, of the solute,  $f$  is the frictional coefficient per solute molecule and  $N_A$  is Avogadro's constant.  $D$ ,  $f$  and  $(\partial\mu/\partial c)_{T,P}$  are all in the general case concentration dependent. The derivative  $(\partial\mu/\partial c)_{T,P}$  is a purely thermodynamic quantity which can be obtained by standard techniques (measurement of osmotic pressure, light scattering, vapour pressure, etc.). Measurement of  $D$  and knowledge of  $(\partial\mu/\partial c)_{T,P}$  thus enables  $f$  and its concentration dependence to be indirectly determined. The determination of  $f$  is the main purpose of the present paper. The frictional coefficient can also be directly determined, for instance, by measuring the self-diffusion coefficient,  $D^+$ , given by<sup>14</sup>:

$$D^+ = \frac{RT}{N_A f} \quad (2)$$

or from measurement of the sedimentation coefficient,  $s$ , defined by<sup>25</sup>:

$$s = \frac{M}{N_A f} (1 - \bar{v}\rho) \quad (3)$$

$R$  is the gas constant,  $M$  and  $\bar{v}$  are the solute molar mass and partial specific volume, respectively, and  $\rho$  is the solution density. It seems reasonable to assume that the frictional coefficient appearing in equations (1) and (2) should be the same but it is not insignificant that this holds also for the frictional coefficient in equation (3). One argument that would support

the view that the sedimentation frictional coefficient should be the same as that for diffusion is that the sedimentation process is so slow in comparison with the energy dissipation from the sedimenting particle into the surrounding medium that on the molecular scale there would be no detectable difference between the processes. This argument seems to be reasonable at moderate concentrations but at more elevated concentrations where the sedimentation process approaches a 'porous plug' situation it may be non-applicable. Although it has earlier been proposed<sup>25,27</sup> that the frictional coefficients operating in diffusion and in sedimentation are the same, some recent experimental studies on polydisperse polymer solutions<sup>5,19,20</sup> indicate the contrary. In the present work there will therefore be an attempt to compare the frictional coefficients from diffusion and sedimentation up to high concentrations for the sharp fractions used here.

For the determination of  $(\partial\mu/\partial c)_{T,P}$  in equation (1) the osmotic pressure,  $\pi$ , has been used and the following relation is introduced to relate  $\pi$  to the derivative of the chemical potential<sup>24</sup>

$$\left( \frac{\partial \mu}{\partial c} \right)_{T,P} = \frac{M(1 - \bar{v}c)}{c} \left( \frac{\partial \pi}{\partial c} \right)_{T,P} \quad (4)$$

For the concentration region discussed in this paper the osmotic pressure can be approximated with sufficient accuracy by a virial expression and instead of equation (1) we obtain for a two component system:

$$D = \frac{RT}{N_A f} (1 - \bar{v}c) (1 + 2\Gamma_2 c + 3\Gamma_3 c^2 + \dots) \quad (5)$$

or to simplify the notation:

$$D = \frac{RT}{N_A f} Q \quad (5a)$$

where the quantity  $Q$  is defined by:

$$Q = (1 - \bar{v}c) (1 + 2\Gamma_2 c + 3\Gamma_3 c^2 + \dots) \quad (6)$$

Comparison of equations (1) and (5a) gives the more general expression:

$$Q = \frac{c}{RT} \left( \frac{\partial \mu}{\partial c} \right)_{T,P} \quad (6a)$$

and it is clear that  $Q$  is essentially the 'thermodynamic' factor.

The virial coefficients  $\Gamma_2, \Gamma_3, \dots$  were obtained from the following polynomial representation of the osmotic pressure data:

$$\pi = a_1 c + a_2 c^2 + a_3 c^3 + \dots \quad (7)$$

using the relations  $\Gamma_2 = a_2/a_1$ ;  $\Gamma_3 = a_3/a_1 \dots$

At infinite dilution equations (5) and (5a) reduce to  $D_0 = (RT)/(N_A f_0)$  giving the following expression for the ratio  $f_0/f$ :

$$f_0/f = (D/D_0) (1 - \bar{v}c)^{-1} (1 + 2\Gamma_2 c + 3\Gamma_3 c^2 + \dots)^{-1} \quad (8)$$

Similarly for sedimentation one can write at infinite

dilution  $s_0 = M(1 - \bar{v}_0\rho_0)/(N_A f_0)$  which for the ratio  $f_0/f$  gives the expression:

$$f_0/f = (s/s_0)(1 - \bar{v}_0\rho_0)/(1 - \bar{v}\rho) \quad (9)$$

The equations (8) and (9) will be used to compare the frictional conditions in diffusion and sedimentation. In this context it could be observed that since the main part of the pressure dependence of the sedimentation coefficient resides in the viscosity, equation (9) is a very good approximation for a calculation of the ratio  $f_0/f$  at atmospheric pressure even if the values of  $s$  and  $s_0$  are not corrected for pressure.

Self-diffusion coefficients have been calculated from:

$$D^+ = D(1 - \bar{v}c)^{-1}(1 + 2\Gamma_2c + 3\Gamma_3c^2 + \dots)^{-1} = D/Q \quad (10)$$

which is a combination of equations (2) and (5) or (5a) assuming the frictional coefficient to be the same in both cases.

Concerning the temperature dependence of the diffusion coefficient, it is seen directly from equation (1) that both the temperature dependence of the frictional coefficient and of the thermodynamic derivative will contribute. Formally, the temperature dependence of  $D$  is given by the following expression, based on kinetic theory:

$$D = D_\infty \exp\left(-\frac{E_D}{RT}\right) \quad (11)$$

where  $D_\infty$  is a numerical parameter independent of temperature ('the diffusion coefficient at infinite temperature') and  $E_D$  the 'activation energy of diffusion transport'. The quantity  $E_D$  will, for a given system, depend upon both concentration and temperature. The temperature dependence of  $E_D$  can be expected to be pronounced in the vicinity of a critical solution temperature. From equation (11) it is clear that by plotting  $\ln D$  versus  $1/T$  certain features of the thermal behaviour of the diffusion coefficient can be analysed.

## EXPERIMENTAL

### Diffusion measurements in Uppsala

Narrow molecular weight distribution standard PS samples with nominal molecular weights  $M = 390\,000$  and  $M = 110\,000$  (manufacturer's data for lots Nos 3b and 4b, respectively) supplied by the Pressure Chemical Company, USA, were used as received. Present data for these samples are  $\bar{M}_{s,D} = 420\,000$  and  $\bar{M}_n = 396\,000^{21}$ ;  $\bar{M}_{s,D} = 112\,000$  and  $\bar{M}_n = 110\,000^{22}$ .

The solvent *trans*-decalin (t-D) was obtained by converting a commercial mixture of the *cis*- and *trans*-isomers into the *trans*-form by use of aluminium chloride and standard techniques. The product was thereafter thoroughly washed with water and finally distilled under reduced pressure over sodium metal in an atmosphere of nitrogen gas. The purity of the t-D used was determined as 99.5% by gas chromatography. Toluene of p.a. grade (Merck) was used without further purification.

All solutions were prepared by weighing. After addition of solvent the polymer was allowed to swell for several days without stirring, and thereafter homogenized by stirring for several days. The solute concentration (mass/volume),  $c$  was

calculated at each temperature,  $t$ , from the weight fraction of solute,  $w$ , and the corresponding solution density,  $\rho(t,w)$ , according to the relation  $c = \rho w$ ; numerical values of  $\rho$  were taken from previous studies<sup>28,29</sup>.

Mutual diffusion coefficients were determined in an apparatus described elsewhere<sup>30</sup>. This apparatus is provided with an air thermostat of special design, which maintains the temperature to within  $\pm 0.01^\circ\text{C}$  over the temperature interval studied. A shear cell for free diffusion measurements described by Claesson<sup>31</sup> was used throughout (see also below).

A boundary was formed between solvent and solution or between two solutions of different solute concentration. The initial concentration difference across the boundary was 10 to 20 kg/m<sup>3</sup>; only a very slight asymmetry could be observed in the spreading boundary. The broadening of the boundary was followed with a *schlieren* optical system and registered photographically. The diffusion experiments lasted about 2 h for PS in toluene and up to 5 h for PS in t-D and the number of exposures varied between 7 and 12 evenly distributed over the time of the experiments. The relatively short time for the experiments is mainly due to that in the *schlieren* method there are certain difficulties in locating the 'base line' when the boundary is too broad. In all the experiments the initial boundary was so sharp that the starting time correction could be taken as zero within the experimental accuracy.

The diffusion coefficients were determined from the *schlieren* patterns on the photographic plate in the following way. The maximum height,  $H$ , of the *schlieren* peak, and the width,  $\Delta x$ , at the height  $H/(e)^{1/2}$ , were measured in a microcomparator (the accuracy of the microcomparator is  $\pm 1\ \mu\text{m}$ ).  $(\Delta x)^2$  was then plotted versus time, and the mutual diffusion coefficient,  $D$ , was determined from the slope of this plot according to the relation<sup>32</sup>  $(\Delta x)^2 = 8Dt$ .

The diffusion coefficients given in Tables 1 and 2 correspond to the average concentration  $\bar{c} = \frac{1}{2}(c_{\text{top}} + c_{\text{bottom}})$  in the boundary. The diffusion coefficient at infinite dilution,  $D_0$ , was obtained by extrapolation of the diffusion coefficients to zero concentration (see Figures 1 and 2).

### Diffusion measurements in Prague

For the diffusion measurements, and the sedimentation measurements (see below) with which they are compared, a different (older) sample also supplied by the Pressure Chemical Company (nominal molecular weight  $M = 110\,000$ ) was used. Thus the data for the two PS samples with the nominal molecular weight  $M = 110\,000$  are not to be expected to be identical (both  $s_0$  and  $D_0$  differed).

The solvent toluene of purity p.a. (Lachema, Brno) was distilled on a column (Berl's saddles, 150 cm). Solutions were prepared volumetrically. 50 ml of solution was sufficient for two subsequent determinations (A and B) of the diffusion coefficient at a given concentration. For further use it was necessary to regenerate the polymer sample several times. Toluene was evaporated in vacuum. The sample was redissolved in benzene (of purity p.a. Lachema, Brno, distilled prior to use) to a concentration of approximately 20% and then quickly frozen in a bath of solid CO<sub>2</sub> in ethanol. Finally benzene was sublimed in vacuum (0.1 mmHg) until the sample attained a constant weight.

Measurements were carried out in a polarization interferometer of the Bryngdahl type<sup>36</sup> using a flowing boundary cell<sup>37</sup>. All the measurements were carried out at  $25^\circ \pm 0.05^\circ\text{C}$ . The apparatus, thermostat, measuring procedure and calculation of the diffusion coefficients have been described else-

Table 1 Results for the system polystyrene/trans-decalin

$t$ (°C)	$\bar{c}$ (kg/m <sup>3</sup> )	$1 - \bar{v}c^a$	$\bar{c}[\eta]^b$	$D(10^{-11} \text{ m}^2/\text{sec})$	$D^+(10^{-11} \text{ m}^2/\text{sec})^c$	$Q$	$f(10^{-10} \text{ Nsec m}^{-1})$	$\frac{\partial \pi}{\partial c} (\text{m}^2/\text{sec}^2)^d$
20.0	0	1	0	0.70	0.70	1.00	5.76	6.13
	2.51	0.998	0.109	0.62 <sub>9</sub>	0.64	0.98	6.34	6.07
	7.46	0.993	0.323	0.61 <sub>5</sub>	0.65	0.95	6.26	5.90
	12.3	0.989	0.533	0.46 <sub>5</sub>	0.51	0.91	7.97	5.70
	14.8	0.986	0.639	0.44 <sub>8</sub>	0.50	0.90	8.09	5.59
	24.5	0.977	1.06	0.27 <sub>3</sub>	0.33	0.83	12.3	5.22
	36.0	0.967	1.56	0.29 <sub>6</sub>	0.37	0.79	10.8	5.05
	51.5	0.953	2.23	0.12 <sub>1</sub>	0.14	0.88	29.3	5.67
	67.0	0.938	2.90	0.13 <sub>2</sub>	0.11	1.15	35.2	7.54
	84.5	0.922	3.66	0.15 <sub>0</sub>	0.089	1.69	45.6	11.27
30.0	0	1	0	0.86	0.86	1.00	4.87	6.37
	6.99	0.993	0.379	0.76 <sub>7</sub>	0.59	1.30	7.09	8.33
	14.2	0.987	0.769	0.75 <sub>6</sub>	0.47	1.61	8.90	10.37
	24.3	0.977	1.32	0.58 <sub>2</sub>	0.28	2.07	14.9	13.50
	36.2	0.966	1.96	0.60 <sub>5</sub>	0.22	2.70	18.6	17.76
	52.0	0.952	2.82	0.49 <sub>1</sub>	0.13	3.71	31.7	24.84
	53.8	0.950	2.92	0.48 <sub>0</sub>	0.13	3.84	33.5	25.73
	67.6	0.937	3.67	0.54 <sub>9</sub>	0.11	4.93	37.6	33.46
	86.7	0.920	4.71	0.59 <sub>0</sub>	0.089	6.60	46.8	45.64
	40.0	0	1	0	1.01	1.00	1.01	4.31
7.33		0.993	0.439	1.02 <sub>5</sub>	0.63	1.64	6.93	10.88
14.5		0.986	0.869	0.99 <sub>0</sub>	0.44	2.25	9.83	15.02
14.5		0.986	0.869	0.97 <sub>7</sub>	0.43	2.25	9.97	15.02
24.1		0.977	1.44	1.04 <sub>2</sub>	0.34	3.08	12.8	20.76
35.4		0.967	2.12	1.03 <sub>8</sub>	0.25	4.13	17.2	28.10
50.6		0.953	3.03	1.00 <sub>2</sub>	0.17	5.74	24.8	39.61
65.8		0.939	3.94	0.95 <sub>8</sub>	0.13	7.61	34.3	53.27
83.0		0.923	4.97	1.03 <sub>2</sub>	0.10	9.99	41.9	71.21

<sup>a</sup> The temperature and concentration dependence of  $\bar{v}$  is obtained from data in a previous work<sup>28</sup>

<sup>b</sup>  $[\eta]$  is taken from ref 23

<sup>c</sup> Calculated from equation (7)

<sup>d</sup> Primary data for the calculations were taken from ref 21 (see main text)

where<sup>37-40</sup>. The previously described registration photometer was modified as follows. A line recorder E1 B1 and a vacuum photocell (Zeiss, Jena) were used in combination with an electric unit (constructed at the institute in Prague) which automatically marked the position of interference maxima and minima.

Experimental results from free diffusion measurements (two subsequent series A and B) are summarized in Table 3. The diffusion coefficients refer to the average concentration  $\bar{c} = \frac{1}{2}(c_{\text{top}} + c_{\text{bottom}})$ , where  $c_{\text{top}}$  and  $c_{\text{bottom}}$  are the concentrations of the solutions used in forming the initial boundary. The concentration difference  $\Delta c$  was chosen in such a manner that three pairs of interference fringes (necessary for the calculation of two values of  $D$ ) could be evaluated. From the data presented in Table 3 the precision of the diffusion coefficients can be estimated to be better than  $\pm 2\%$ .

#### Comments on diffusion measurements in concentrated solutions

The handling of concentrated macromolecular solutions is usually difficult due to their high viscosity. This necessitates extreme care in all types of accurate measurements. For instance, even minute evaporation may introduce sufficient inhomogeneities in density to cause very disturbing convections and even affect the interferometric recording of a concentration gradient. Transport experiments are particularly sensitive in this respect and great care has been exercised in this work to avoid such sources of error.

In the present study two different boundary formation

techniques for diffusion can be compared, namely the shear cell and flowing junction methods. The Claesson shear cell<sup>31</sup> gives extremely sharp initial boundaries but can sometimes give rise to leakage problems for dilute low viscosity solutions. However, at elevated concentrations all leakage is virtually eliminated due to high viscosity and furthermore, in good solvents, the rate of diffusion is increased considerably which means that the time for an experiment can be decreased. All these features make the cell ideally suited for diffusion studies on concentrated macromolecular solutions. In the flowing junction cell the sharpening of the initial boundary depends on the matching of flows of the upper and lower solution. When concentration is increased the time lag of the solution flow can become considerable and the technique is then to form the boundary slowly and in steps carefully observing the shape of the fringes close to the boundary. Since the Bryngdahl type interferometer gives a point to point image of the cell at the position of the photographic plate visual inspection of the interference pattern is a very sensitive way of detecting even minute errors in the boundary formation. All results reported here have been free from such errors.

#### Sedimentation measurements

Ultracentrifugation of the system PS(110 000)/toluene (see Table 2 below) was carried out at 25°C using an MSE analytical ultracentrifuge (Centriscan 75) equipped with a temperature controlling unit, electronic speed control and a *schlieren* system of the photoelectric scanning type<sup>33,34</sup> to

Table 2 Results for the system polystyrene ( $M = 110\,000$ )/toluene at  $25^\circ\text{C}^a$ 

(a) Free diffusion measurements						
$\bar{c}$ (kg/m <sup>3</sup> )	$1 - \bar{v}\bar{c}^b$	$\bar{c}[\eta]^c$	$D$ ( $10^{-11}$ m <sup>2</sup> /sec)	$D^+$ ( $10^{-11}$ m <sup>2</sup> /sec)	$Q$	$f$ ( $10^{-11}$ Nsec m <sup>-1</sup> )
0	1	0	4.25	4.25	1.00	9.68
3.89	0.996	0.200	4.69	3.02	1.55	13.6
13.0	0.988	0.666	5.20	1.71	3.04	24.1
24.7	0.977	1.27	6.75	1.25	5.40	32.8
38.7	0.964	1.99	7.61	0.87	8.75	47.5
53.0	0.951	2.72	8.75	0.68	12.9	60.1
66.5	0.939	3.41	10.0	0.59	16.9	69.9
86.9	0.917	4.46	11.3	0.47	24.0	87.1
115.5	0.894	5.93	13.0	0.37	35.1	109.8

(b) Velocity sedimentation measurements				
$c$ (kg/m <sup>3</sup> )	$\frac{1 - \bar{v}_0\rho_0^b}{1 - \bar{v}\rho}$	$c[\eta]^c$	$s$ ( $10^{-13}$ sec)	$f$ ( $10^{-11}$ Nsec m)
0	1	0	4.00	9.69
1.58	1.000	0.081	3.45	11.2
2.80	1.001	0.144	3.20	12.1
6.39	1.004	0.328	2.50	15.4
9.04	1.007	0.464	2.24	17.3
12.86	1.010	0.660	1.84	21.0
18.52	1.015	0.950	1.49	25.5
21.01	1.018	1.08	1.39	27.7
30.44	1.027	1.56	1.05	35.9
35.21	1.032	1.81	0.92 <sub>0</sub>	40.4
54.80	1.051	2.81	0.63 <sub>7</sub>	57.0
72.96	1.070	3.74	0.50 <sub>8</sub>	69.2
89.03	1.088	4.57	0.39 <sub>9</sub>	88.9
125.2	1.130	6.42	0.27 <sub>0</sub>	127.9

<sup>a</sup> Measurements performed in Uppsala

<sup>b</sup>  $\bar{v}$  is taken from ref 29

<sup>c</sup>  $[\eta] = 0.051_3$  m<sup>3</sup>/kg

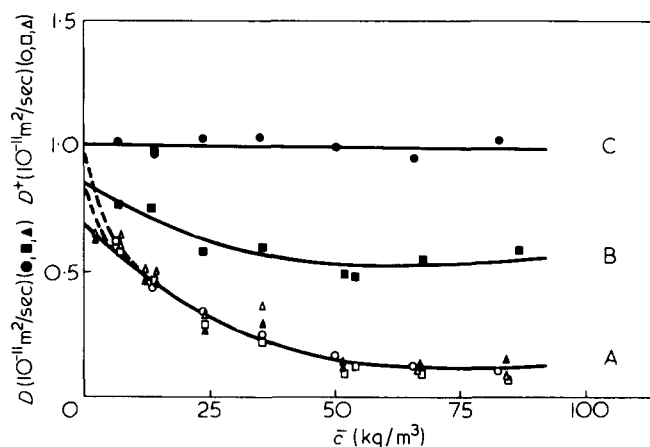


Figure 1 Concentration dependence of the mutual diffusion coefficient ( $D$ ) and the calculated self-diffusion coefficient ( $D^+$ ) from equation (10) for the system PS/*trans*-decalin at temperatures: A,  $20^\circ\text{C}$ ; B,  $30^\circ\text{C}$ ; C,  $40^\circ\text{C}$ . The broken curves indicate the concentration dependence of  $D^+$  at low concentrations ( $D^+$  extrapolates to  $D_0$ )

record the position of the sedimenting boundary. All the experiments were performed at a rotor speed of 60 000 rpm.

The sedimentation data for the 'older' PS sample ( $M \approx 110\,000$ ) in toluene with which the diffusion results from Prague are compared, were obtained from experiments performed in an oil-turbine ultracentrifuge of the Svedberg

type<sup>25</sup>. The experiments were performed at a rotor speed of 54 000 rpm and at temperatures between  $23^\circ$  and  $24^\circ\text{C}$ , however, all data have been corrected to  $25^\circ\text{C}^{25}$ .

The experiments and the calculations were performed in accordance with principles discussed recently<sup>35</sup>.

## RESULTS AND DISCUSSION

The results of the measurements are collected in Tables 1–3 and in Figures 1–8. To a large degree the Tables and Figures are self-explanatory and therefore the discussion will be concentrated on the main features of the results namely: (a) concentration and temperature dependence of the diffusion coefficient,  $D$ ; (b) concentration and temperature dependence of the frictional coefficient,  $f$ , and of the thermodynamic factor; (c) calculated self-diffusion coefficients; (d) comparison between diffusion and sedimentation frictional coefficients.

From Table 2 and Figure 2 it is clear that in the good solvent toluene at  $25^\circ\text{C}$ ,  $D$  increases considerably and almost linearly (some downward concavity) over the concentration interval studied. The data from Prague (Table 3) although valid for a slightly different PS sample and obtained by a different experimental technique show very similar features. In the solvent *trans*-decalin, on the other hand, which in the temperature interval  $20^\circ$ – $40^\circ\text{C}$  is a less good solvent ( $\theta = 20.8^\circ\text{C}$ ),  $D$  varies less with concentration, the variation being strongly temperature dependent (Figure 1 and Table 1)

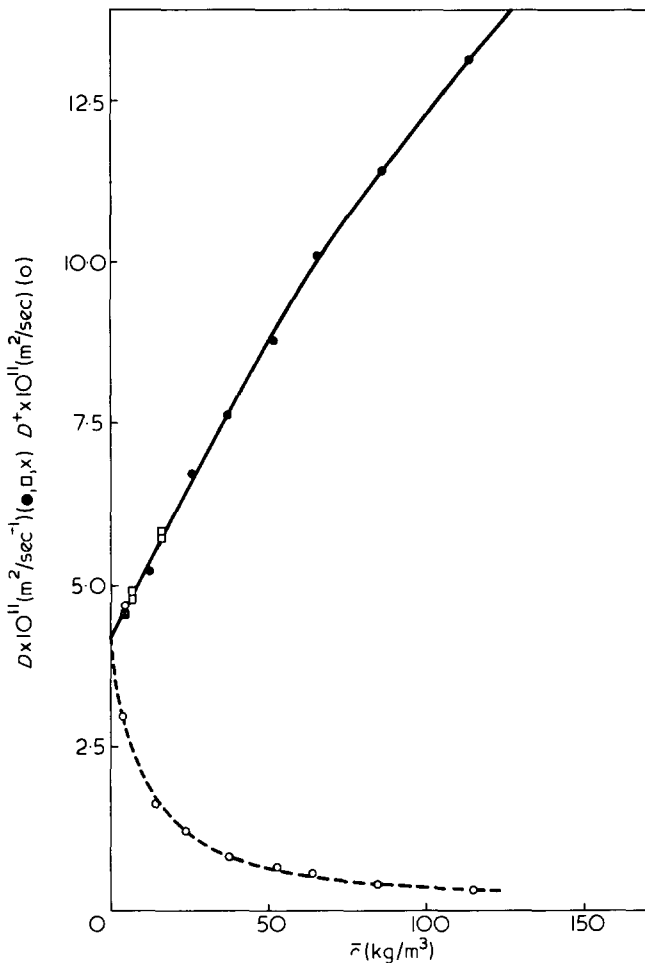


Figure 2 Concentration dependence at 25°C of the mutual diffusion coefficient ( $D$ ) and the calculated self-diffusion coefficient ( $D^+$ ) from equation (10) for the system PS ( $M = 110\,000$ )/toluene: ●, ○, this work (Uppsala); □, inelastic laser light scattering data for the system PS ( $M = 110\,000$ )/toluene taken from ref 4; x, measured with a Rayleigh interferometer technique<sup>48</sup>

At temperatures below 40°C,  $D$  first decreases with increasing concentration and then attains an almost constant value or passes through a shallow minimum. The same tendency has been reported for the system polystyrene/cyclohexane at temperatures below and in the neighbourhood of the  $\theta$  temperature<sup>1,2</sup>. These features can be explained<sup>1,2</sup> in terms of thermodynamic and hydrodynamic arguments. According to equation (1) (see equations 5 and 5a), the mutual diffusion coefficient can be divided into a 'thermodynamic' and a 'hydrodynamic' factor,  $Q(c)$  and  $1/f(c)$ , respectively. It is the interplay between these two quantities and their concentration and temperature dependence that determine the value of diffusion coefficient  $D$ .

It is clear from equations (1), (4) and (6a) that osmotic pressure data<sup>21,22</sup> enables the calculation of the 'thermodynamic' factor  $Q$  which in combination with measured values of  $D$  gives the frictional coefficient,  $f$ . Such data have been collected in Tables 1 and 2.

If the osmotic pressure,  $\pi$ , is expanded as a power series in  $c$  (see equation 7), the best least squares fit to the experimental data for the system PS/t-D gives the following expressions at the actual temperatures ( $\pi$  is expressed in Pa and  $c$  in  $\text{kg/m}^3$ )

$$\begin{aligned} \pi = & 6.133c - 1.055 \times 10^{-2}c^2 - 5.677 \times 10^{-4}c^3 \\ & + 1.174 \times 10^{-5}c^4 - 3.624 \times 10^{-8}c^5 \quad (20^\circ\text{C}) \end{aligned}$$

$$\begin{aligned} \pi = & 6.371c + 14.226 \times 10^{-2}c^2 - 3.148 \times 10^{-4}c^3 \\ & + 1.520 \times 10^{-5}c^4 - 6.350 \times 10^{-8}c^5 \quad (30^\circ\text{C}) \\ \pi = & 6.620c + 29.51 \times 10^{-2}c^2 - 6.075 \times 10^{-4}c^3 \\ & + 1.935 \times 10^{-5}c^4 - 6.784 \times 10^{-8}c^5 \quad (40^\circ\text{C}) \end{aligned}$$

The analogous expansion coefficients for the system PS/toluene are evaluated from data in ref 22. It is clear from the Tables that the thermodynamic quantity  $Q(c)$ , calculated from the osmotic data<sup>21,22</sup> shows a very strong concentration dependence for the system PS/toluene. In the system PS/t-D the concentration dependence of  $Q(c)$  is considerable at 40°C but decreases with decreasing temperature and becomes small (passes through a shallow minimum) at 20°C (see also Figure 5b).

The frictional coefficients calculated from equation (5a) for known values of  $D$  and  $Q$  [ $Q(c)$  is calculated for the average concentration  $c = \bar{c}$  of the diffusion experiments], see Tables 1 and 2, have been plotted in Figures 3 and 4 in a 'hydrodynamically normalized' form. It has previously been

Table 3 Experimental results from diffusion measurements at 25°C for the system PS ( $M \approx 110\,000$ )/toluene<sup>a</sup>

$c$ (kg/m <sup>3</sup> )	$\Delta c$ (kg/m <sup>3</sup> )	$D$ (10 <sup>-11</sup> m <sup>2</sup> /sec)			$\frac{\Delta D}{D_{\text{ave}}} \times 10^2$
		Series A	Series B	Average	
0				4.50	
0.489	0.977	4.43	4.71	4.57	6.0
0.494	0.988	4.60	4.57	4.58	0.7
4.91	0.979	5.16	5.13	5.15	0.5
9.90	1.03	5.86	6.01	5.93	2.4
20.1	1.02	7.08	7.06	7.07	0.2
40.1	1.01	8.94	9.21	9.08	2.9
49.8	0.979	10.34	9.79	10.06	5.5
69.9	0.980	11.49	11.41	11.45	0.7
85.6	0.982	12.33	12.37	12.35	0.3
100.6	1.09	13.21	13.34	13.28	1.0
121.0	1.08	13.81	14.43	14.12	4.3

<sup>a</sup> Measurements performed in Prague

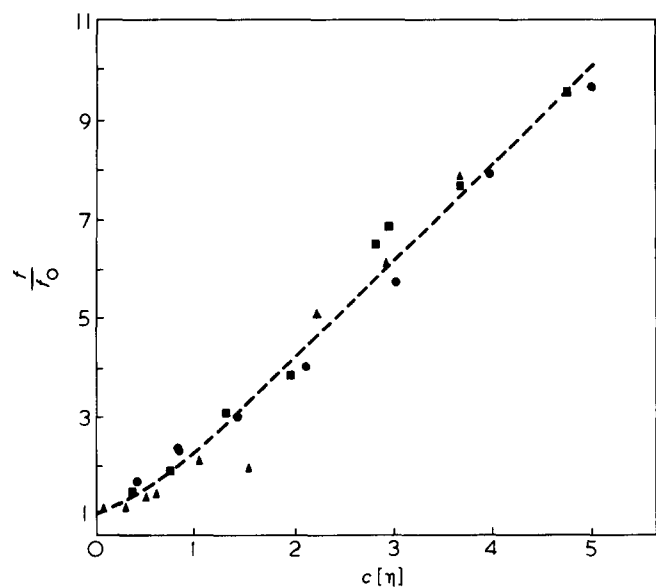
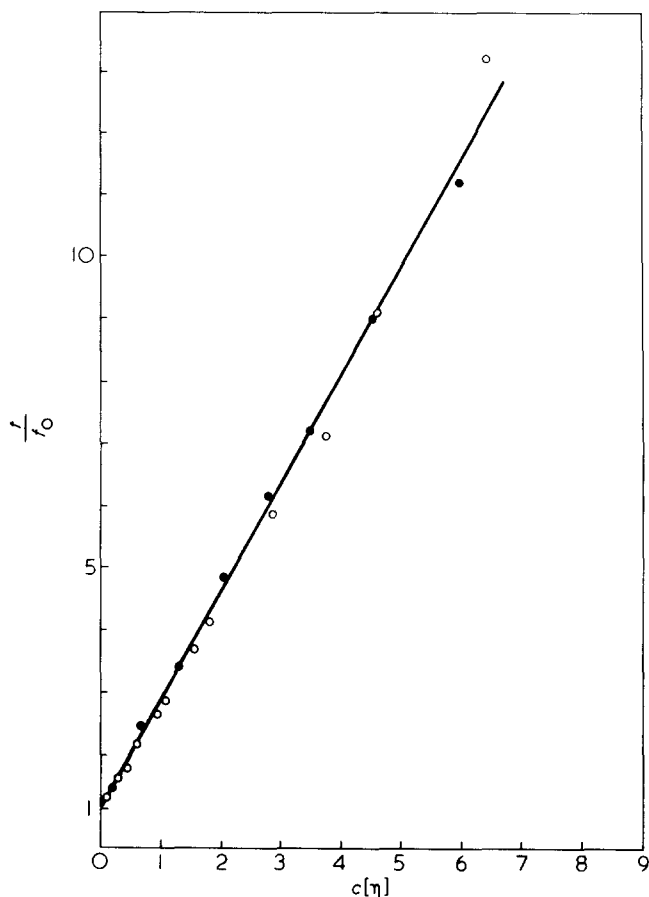


Figure 3 Plot of  $f/f_0$  versus  $c[\eta]$  for the system PS ( $M = 390\,000$ )/trans-decalin at the temperatures: ▲, 20.0°C; ■, 30.0°C; ●, 40.0°C



Plot 4 Plot of  $f/f_0$  versus  $c[\eta]$  at 25°C for the system PS ( $M = 110\,000$ )/toluene: ●, calculated from mutual diffusion and osmotic pressure data (equation 5); ○, calculated from velocity sedimentation data (equation 9) (see Table 2)

shown that the 'hydrodynamically normalized' plot<sup>41</sup> of  $s_0/s$  versus  $c[\eta]$  is sensitive to details in the transport process. Figures 3 and 4 constitute analogous plots of  $f/f_0$  versus  $c[\eta]$  which further illustrate the transport properties over the concentration and temperature regions investigated. For the system PS/toluene Figure 4 shows that the frictional coefficient is a linear function of concentration over the entire composition range studied. From Figure 3 it is evident that also for the system PS/t-D the frictional coefficient is to a very good approximation a linear function of concentration with the same relative change irrespective of temperature (although the 'thermodynamic' factor  $Q$  shows a considerable sensitivity to temperature). Although the broken line in Figure 3 is slightly concave upwards for low values of  $c[\eta]$ , the basic feature is the almost linear increase of  $f/f_0$  with  $c[\eta]$  which is similar to that obtained from recent velocity sedimentation measurements on the same system<sup>23</sup> as well as on other systems<sup>19,41</sup>. However, the detailed characteristics observed from the velocity sedimentation results cannot be discerned from the data presented in Figure 3. This is probably due to the relatively large experimental errors in the data from the combined diffusion and osmotic pressure measurements compared with those from sedimentation. Since the values of the mutual diffusion coefficients are low (high solvent viscosity) ( $<1.10^{-11}$  m<sup>2</sup>/sec) they can be assumed to be marred by relatively large errors; moreover, the osmotic pressure data may also contain minor errors. Such errors could be magnified in a system close to phase separation and are probably the reason for the relative large scatter of the experimental points in Figure 3.

The almost linear relationship between  $f/f_0$  and  $c[\eta]$ , as shown in Figures 3 and 4, indicates that to a very good approximation one can write:

$$\frac{f}{f_0} = 1 + k'_f c[\eta] \quad (12)$$

or

$$f = f_0(1 + k'_f c[\eta]) \quad (12a)$$

The data shown in Figures 3 and 4 give  $k'_f \approx 2$  for both systems. The temperature dependence of  $f$  is thus closely related to the temperature dependence of  $[\eta]$  ( $k'_f$  can be assumed to vary only slightly if at all with a change in temperature). Since  $f_0 \sim \eta_0 [\eta]^{1/3}$  the temperature variation of  $f_0$  also includes the temperature dependence of the solvent viscosity,  $\eta_0$ . Expressions (12) and (12a) show that the

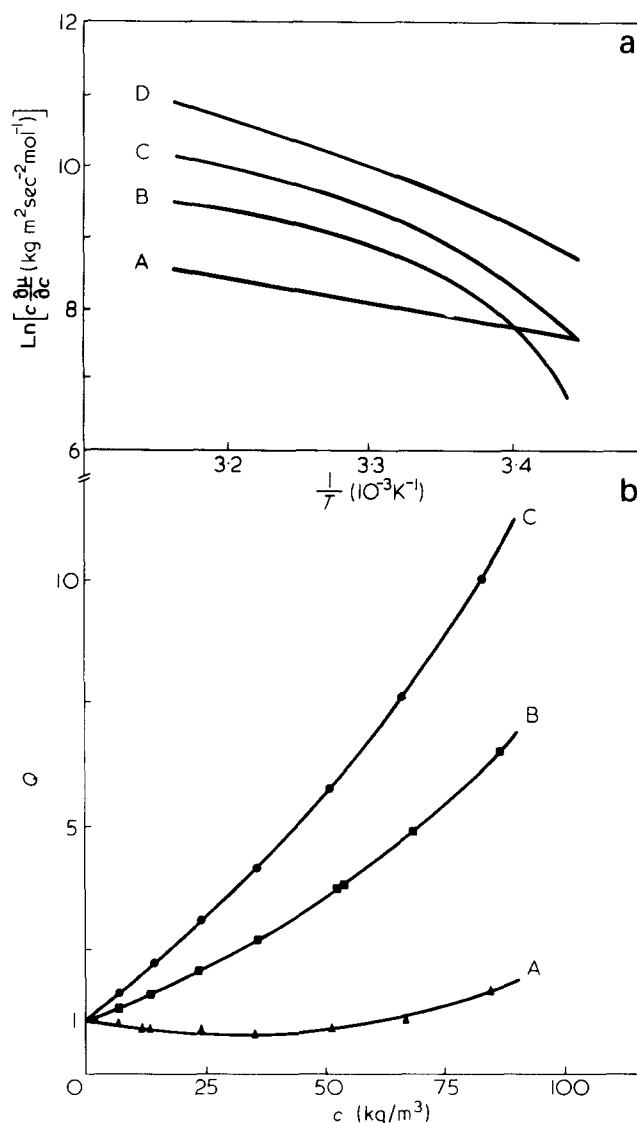
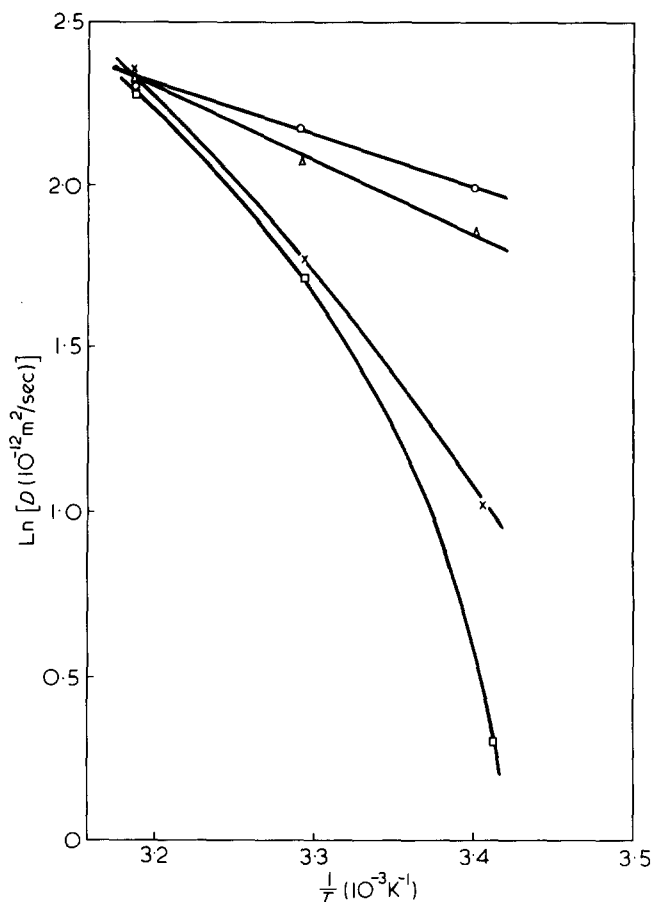


Figure 5 (a) Temperature dependence of the thermodynamic factor calculated from osmotic pressure data (see Table 1) for the system PS/trans-decalin for the approximate concentrations: (A) ~9 kg/m<sup>3</sup>; (B) ~42 kg/m<sup>3</sup> (C) ~73 kg/m<sup>3</sup> (D) ~131 kg/m<sup>3</sup>. Note that according to equation (6a)  $RTQ = c(\partial\mu/\partial c)$ . The  $\theta$  temperature ( $\theta = 20.8^\circ\text{C}$ ) corresponds to  $1/T = 3.40 \times 10^{-3} \text{K}^{-1}$ . (b) The factor  $Q$  for the system PS/trans-decalin calculated from equation (6) plotted versus the concentration ( $c$ ) at temperatures: A, 20°C; B, 30°C; C, 40°C



**Figure 6** Temperature dependence of the mutual diffusion coefficient for the system PS/*trans*-decalin for the approximate concentrations:  $\circ$ ,  $0 \text{ kg/m}^3$ ;  $\triangle$ ,  $\sim 7 \text{ kg/m}^3$ ;  $\times$ ,  $\sim 25 \text{ kg/m}^3$ ;  $\square$ ,  $\sim 67 \text{ kg/m}^3$ . From the data in *Figure 1* and *Table 1* it is evident that in the concentration interval studied from approximately  $50 \text{ kg/m}^3$  and upwards the temperature variation of  $D$  does not change much (i.e. the points  $\square$  are representative for this interval)

temperature variation of  $f/f_0$  and  $f$  is concentration dependent through the term  $k_f c[\eta]$  and thus this temperature dependence increases with concentration.

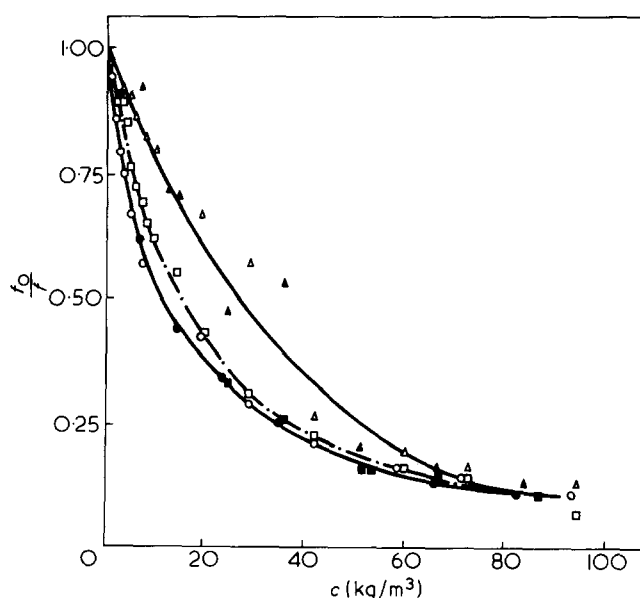
The temperature dependence of the thermodynamic factor  $c(\partial\mu/\partial c)$  in equation (1) (see also equation 6a), is demonstrated in *Figures 5a* and *5b* (for the system PS/t-D). At higher temperatures this factor increases smoothly with increasing concentration. When lower temperatures are approached (phase separation is approached), however, the factor  $c(\partial\mu/\partial c)$ —or  $Q$ —shows a marked tendency to decrease at low values for intermediate concentrations (curves B and C in *Figure 5a*). An explanation for this behaviour is that the lowest and the highest concentrations are relatively far from the region where the phase equilibrium curve has its maximum, whereas the intermediate concentrations are located in this region where  $\partial\mu/\partial c$  for general thermodynamic reasons will approach zero as the temperature decreases<sup>42</sup>. For the lowest temperature the thermodynamic factor  $Q$  will thus pass through a minimum when the concentration is increased from infinite dilution up to the highest values investigated (see *Figure 5b*).

From the diffusion data in *Table 1* (PS/t-D) it can be observed that the diffusion coefficient at a given concentration increases with increasing temperature; this increase is more pronounced for the higher concentrations. From the plots of  $\ln D$  versus  $1/T$  shown in *Figure 6* (using equation (11) for a number of concentrations)  $E_D$  can be calculated.

At infinite dilution  $E_D$  has been determined to  $13.7 \text{ kJ/mol}$ , in good agreement with  $13.1 \text{ kJ/mol}$ , reported previously for the same polymer–solvent system<sup>43</sup>. The apparent activation energy depends on the composition of the system and on the nature of the solvent<sup>44</sup>. For the present system,  $E_D$  increases with increasing concentration. This behaviour has also been observed for other polymer–solvent systems<sup>2,6,45</sup>. For the higher temperatures (far from  $\theta = 20.8^\circ \text{C}$ ) the increase of  $E_D$  levels off at sufficiently high concentrations (see *Figure 6*) whereas for temperatures in the vicinity of the  $\theta$  temperature the increase of  $E_D$  prevails up to the highest concentrations. The temperature dependence of the thermodynamic factor has been plotted in *Figure 5a* in a way which allows direct comparison with the temperature dependence of the diffusion coefficient according to *Figure 6*. It is interesting to note from *Figures 5a* and *6* that the temperature dependence of the diffusion coefficient is similar to that of the thermodynamic factor. This indicates that the apparent activation energy,  $E_D$ , which can be regarded as a sum of a hydrodynamic and a thermodynamic term has as temperature dependence which is due mainly to the temperature dependence of the thermodynamic factor.

Depending upon the conditions under which the diffusion takes place, translational diffusion of a molecule is described by two different coefficients; the mutual diffusion coefficient,  $D$ , characterizing the relaxation of a concentration gradient, and the self-diffusion coefficient,  $D^+$ , characterizing the random motions of an individual solute molecule in the absence of a concentration gradient. The concentration dependence of both  $D$  and  $D^+$  (calculated from equation 10) is illustrated in *Figures 1* and *2* (see also *Tables 1* and *2*).

For the system PS/t-D (*Figure 1*) the following features can be observed. At  $20^\circ \text{C}$  the concentration dependence of  $D$  and  $D^+$  can be represented by the same curve. For the other temperatures  $D^+$  falls off more rapidly with increasing concentration than does the mutual diffusion coefficient, and very soon these curves merge into that at  $20^\circ \text{C}$ . The observed difference between the mutual diffusion coefficient and the self-diffusion coefficient at temperatures far from



**Figure 7** Concentration dependence of  $f_0/f$  for the system PS/*trans*-decalin calculated from mutual diffusion and osmotic pressure data (equation 8);  $\triangle$ ,  $20.0^\circ \text{C}$ ;  $\blacksquare$ ,  $30.0^\circ \text{C}$ ;  $\bullet$ ,  $40.0^\circ \text{C}$ ; and from velocity sedimentation data (equation 9):  $\triangle$ ,  $20.0^\circ \text{C}$ ;  $\square$ ,  $30.0^\circ \text{C}$ ;  $\circ$ ,  $40.0^\circ \text{C}$



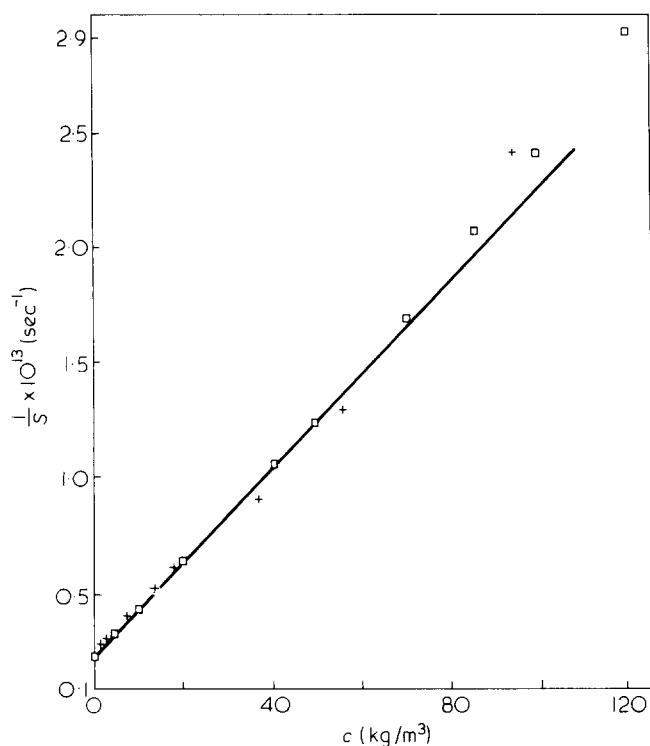


Figure 8 Plot of sedimentation data for the system PS ( $M \approx 110\,000$ )/toluene at 25°C (see Table 3).  $\square$ , calculated from diffusion measurements performed in Prague; +, sedimentation data obtained in Uppsala, see the main text sections 'Experimental' and 'Results and Discussion' for details

the  $\theta$  temperature is described by equation (10). There are reports for various polymer-solvent systems<sup>8,9,12,20</sup> which show essentially the same feature, namely that the self-diffusion coefficient is substantially less than the mutual diffusion coefficient in all but the most dilute solutions. On the other hand, for a thermodynamically good system, PS in toluene (see Figure 2), the mutual diffusion coefficient increases strongly with increasing concentration indicating that the thermodynamic factor dominates over the hydrodynamic factor (see Discussion above). It should be noted that the curve is initially linear but gradually becomes concave downwards, in agreement with previous observations for the same polymer-solvent system<sup>1,2</sup>. The calculated self-diffusion coefficient falls off rapidly to attain an almost constant value at higher concentrations (see Figure 2). This tendency is consistent with that for PS/t-D.

For concentrated aqueous solutions of dextran<sup>5</sup>, poly(ethylene glycol)<sup>5</sup>, bovine serum albumin<sup>20</sup> and hydroxyl propyl cellulose<sup>19</sup> it has recently been found experimentally that the frictional coefficient calculated from osmotic pressure and diffusion data differs noticeably from that calculated from velocity sedimentation data. The ratio  $f_0/f$  determined from sedimentation was observed to decrease more rapidly with increasing concentration than  $f_0/f$  evaluated from diffusion and osmotic pressure. Furthermore, for dextran in concentrated aqueous solutions the combination of mutual diffusion and self-diffusion data<sup>8</sup> gave values of the thermodynamic factor in equation (10) that differed from the osmotically-determined parameters. The difference was explained<sup>8</sup> by the finite width of the molecular weight distribution and the increasing importance of the *type of average* used in the calculations when the concentration was increased. In the present investigation the polymer fractions used were characterized by such narrow molecular weight distributions that all coefficients (diffusion, frictional, virial, etc.) could be taken as valid for a definite molecular weight,

thus avoiding the difficulty with averages. The present data of  $f_0/f$  for the system PS/t-D ( $f_0/f$  was evaluated from equations (8) and (9), respectively), as plotted in Figure 7, show that the values of  $f_0/f$  obtained from equation (8) are within experimental error (see the scatter of points in Figure 3) in fair agreement with those calculated from equation (9).

In Figure 4 similar data are shown for the system PS/toluene and one can see that the ratio  $f/f_0$  calculated from combined diffusion and osmotic pressure data (equation 8) and that calculated from sedimentation data (equation 9), (Table 2) can be represented by the same straight line over the entire  $c[\eta]$ -interval with very little scatter. Figure 8 gives data for another system PS/toluene from diffusion measurements in the Prague laboratory and sedimentation measurements in the Uppsala laboratory (see Experimental). From the diffusion measurements (see Table 3) combined with osmotic pressure data<sup>22</sup> values of  $1/s$  were calculated from a combination of equations (5) and (3) and plotted together with the values of  $1/s$  directly obtained from the sedimentation experiments. Figure 8 shows that there is a good agreement between these two sets of data.

The data presented in Figures 4, 7 and 8 seem to imply that the concentration dependence of the frictional coefficient in sedimentation is the same as that operating in diffusion and that for random coil macromolecules the frictional coefficients operating in sedimentation and diffusion are equal over the entire concentration region studied. Conclusions about the general validity of this observation must, however, be founded on further studies.

It seems reasonable that the earlier observed inequality between diffusion and sedimentation friction for the water-soluble macromolecules may be explained by the polydispersity of the samples. The dextran<sup>5</sup>, poly(ethylene glycol)<sup>5</sup> and hydroxypropyl cellulose<sup>19</sup> samples were all polydisperse. For bovine serum albumin recent inelastic laser light scattering measurements on moderately concentrated solutions have indicated that the solutions were polydisperse<sup>9,46</sup>. This observation is in agreement with previous electron microscope<sup>47</sup> and separation column<sup>48</sup> investigations which indicated the presence of dimers, trimers and larger aggregates. Furthermore, the presence of electrostatic charge effects may also influence the measurements<sup>46</sup>.

The results in this paper also show that the thermodynamic properties of a concentrated macromolecular system can often conveniently be determined with sufficient accuracy by a combination of diffusion and velocity sedimentation measurements.

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