Hydrodynamic properties of linear poly(dimethyl siloxanes) in bromocyclohexane at the theta temperature

Jitka Horská, Vladimír Petrus and Miloslav Bohdanecký
Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences,
162 06 Prague 6, Czechoslovakia

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Hydrodynamic quantities (sedimentation coefficients $s^{\circ}_{0,\theta}$, and intrinsic viscosities $[\eta]_{\theta}$, in bromocyclohexane at 310 K) and weight-average molecular weights (by light scattering) have been measured for poly(dimethyl siloxane) fractions ($45 \leqslant M_w \times 10^{-3} \leqslant 300$). The ratio $[\eta]_{\theta}/s^{\circ}_{0,\theta}$ was found to be invariant with respect to M, and the value of $(\langle R^2\rangle_0/M)_{\infty}$ (where $\langle R^2\rangle_0$ is the mean-square end-to-end distance) computed from $[\eta]_{\theta}/s^{\circ}_{0,\theta}$ was in good agreement with that found by other methods. It is concluded that the translational friction behaviour is similar to that of other flexible chain polymers and that anomalies indicated by some authors are due to inaccuracies in experimental data.

(Keywords: linear poly(dimethyl siloxanes); sedimentation coefficients; intrinsic viscosities; unperturbed dimensions; theta conditions)

INTRODUCTION

According to the theory of the hydrodynamic properties of linear non-draining Gaussian coils under θ conditions, the intrinsic viscosity $[\eta]_{\theta}$ and intrinsic translational friction coefficient $[f]_{\theta}$ are related to the molecular weight M and the unperturbed mean-square end-to-end distance $\langle R^2\rangle_0$ by the equations

$$[\eta]_{\theta} = \Phi_{0,\infty}(\langle R^2\rangle_0/M)^{3/2}_{\infty}M^{1/2} \tag{1}$$

$$[f]_{\theta} = f_{0,\theta}/\eta_0 = P_{0,\infty}(\langle R^2\rangle_0/M)^{1/2}_{\infty}M^{1/2} \tag{2}$$

where $\Phi_{0,\infty}$ and $P_{0,\infty}$ are universal constants[1], $f_{0,\theta}$ is the translational friction coefficient, and η_0 is the solvent viscosity. The friction coefficient is obtained from the sedimentation coefficient $s^{\circ}_{0,\theta}$ (at unit pressure and zero concentration) or from the diffusion coefficient $D_{0,\theta}$ (at zero concentration) by means of the equations

$$f_{0,\theta} = [(1-\bar{v}\rho_0)/N_A]M/s^{\circ}_{0,\theta} \tag{3}$$

and

$$f_{0,\theta} = kT/D_{0,\theta} \tag{4}$$

where ρ_0 is the solvent density, $\bar{v}$ is the partial specific volume of the solute, N_A is the Avogadro number, k is the Boltzmann constant and T is the temperature (in K). According to equations (1) to (4), the intrinsic viscosity, friction coefficient and sedimentation coefficient under θ conditions should be proportional to $M^{1/2}$, and the diffusion coefficient should be proportional to $M^{-1/2}$.

Available data for poly(dimethyl siloxane) (PDMS) at $M > 4 \times 10^4$ in bromocyclohexane (BrCHX) at $\theta = 301$ K are not fully consistent with this, as commented upon, for example, in ref. 2. While, in correspondence with theory, the second virial coefficient is zero and the intrinsic viscosity is proportional to $M^{1/2}$, the diffusion coefficients, particularly their dependence on M, seem to indicate an excluded-volume effect[3,4]. No exceptions of this type have been reported so far.

Data on the translational friction coefficient for high-molecular-weight PDMS in BrCHX are scarce. We decided therefore to investigate this problem in more detail and verify if the anomaly mentioned above does exist. We determined the friction coefficients by sedimentation rather than diffusion measurements because, at high molecular weights, the former method yields data of higher accuracy.

EXPERIMENTAL

Polymer and solutions

Fractions of linear PDMS, provided by courtesy of the Department of Chemistry, University of York (England), were prepared from a commercial sample (Dow Corning, DC-200) by preparative g.p.c. The method has been described earlier[5]. According to the g.p.c. analysis, the molecular weight distribution is narrow, M_w/M_n being ~ 1.2.

Solvents (analytical grade) were distilled before use and their purity (according to gas chromatography) was better than 99.5%. Water content in bromocyclohexane (lower than 0.15%) was determined by the standard Fischer method.

Polymer solutions were prepared by weighing both polymer and solvent and the volume concentration (in g cm^{-3}) was calculated by means of density values. Density of bromocyclohexane ($\rho_0 = 1.3295_0$ at 298 K and 1.3259_0 at 301 K) was determined in a modified Sprengel–Ostwald pycnometer; values of partial specific volume of PDMS were taken from literature[6,7].

The polymer was dissolved by shaking in sealed ampoules at 310–320 K (BrCHX) and at 298 K (toluene) for about

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24 h. Measurements were carried out at 298 K in toluene and at 301 K in bromocyclohexane.

Viscometry

The viscosity of PDMS solutions in BrCHX at 301 K was measured in Ubbelohde capillary viscometers adapted for dilution (capillary diameter 0.47 mm and length 110 mm) and equipped with an electro-optical device for recording flow times with a precision of ±0.05 s. Polymer concentrations were chosen so that the specific viscosity was between 0.15 and 0.80. The temperature was maintained with an accuracy better than ±0.01 K. The intrinsic viscosity and the Huggins coefficient were obtained by the Heller method[8] from the specific viscosity for five concentrations. Kinetic energy corrections were negligible. The results are given in *Table 1*.

The viscosity of bromocyclohexane at 301 K, $\eta_0 = 1.92 \times 10^{-2}$ P, was determined in a capillary viscometer calibrated with water and benzene. It agrees with the value, $\eta_0 = 1.91 \times 10^{-2}$ P, obtained by interpolating the dependence of $\ln \eta_0$ vs. $1/T$ based on reported data[9]. Both values are much higher than those given by Haug and Meyerhoff[6] ($\eta_0 = 1.3 \times 10^{-2}$ P), and by Adank and Elias[10] ($\eta_0 = 1.115 \times 10^{-2}$ P).

Light scattering

The static light scattering (LS) data were obtained from measurements on a commercial FICA instrument (France) with unpolarized light at $\lambda_0 = 546$ nm. The temperature was maintained with an accuracy of ±0.2 K. Solutions (concentration 0.2–1.0%) were measured in low-volume cells (about 3.5 cm^3). Before measurement, solutions were clarified by filtration through a heated glass filter (porosity G 5) under pressure of nitrogen ($p \simeq 0.1$ atm). The refractive index increment of PDMS in bromocyclohexane at 301 K used in this study ($dn/dc = -0.825$ cm^3 g^{-1}) was the arithmetic mean from values reported[10] for $M > 30 \times 10^3$. The reported value[11] for toluene at 298 K ($dn/dc = -0.0933$ cm^3 g^{-1}) was verified using the Brice–Phoenix BP 2000-V differential refractometer; we found $dn/dc = -0.0938 \pm 0.001$ cm^3 g^{-1}, in good agreement with the above value. The angular and concentration dependences of scattered light (at 30–150°) were plotted by the standard Zimm procedure.

Quasielastic light scattering (QELS) was used to check qualitatively the presence of high-molecular-weight particles in solutions. The instrument (photon correlation spectrometer) has been described earlier[12].

Sedimentation analysis

The sedimentation coefficients of PDMS in BrCHX were determined in the Spinco E-HT analytical ultracentrifuge (rotor An-E, 50740 r.p.m.) from measurements at four concentrations ($(2\text{–}12) \times 10^{-3}$ g cm^{-3}). When investigating the presence of high-molecular-weight particles in solutions, we used higher concentrations (4×10^{-2} g cm^{-3}). The temperature was maintained during each run using the RTIC system with an accuracy better than ±0.1 K.

Table 1 Experimental results for PDMS in BrCHX at 301 K

Sample	$M \times 10^{-3}$	$s^{\circ}_{0,\theta} \times 10^{13}$ (S)	$[\eta]_\theta$ (dl g^{-1})	$k_{s,\theta}/[\eta]_\theta$ (g dl^{-1})	$k_{H,\theta}$
1	317^b	3.91	0.439	0.56	0.55
2	285^a	3.38	0.381	0.55	0.46
3	213^b	3.23	0.360	0.60	0.47
4	183^a	2.99	0.333	0.53	0.49
5	90.8^b	2.14	0.235	0.46	0.45
6	98^a	2.08	0.232	0.57	0.48
7	45.4^b	1.51	0.166	0.63	0.59

[a] M_w from light scattering in toluene

[b] M_η calculated from $[\eta]_\theta$ according to $[\eta]_\theta = 0.78 \times 10^{-3} M_\eta^{0.5}$ ($[\eta]_\theta$ in dl g^{-1})

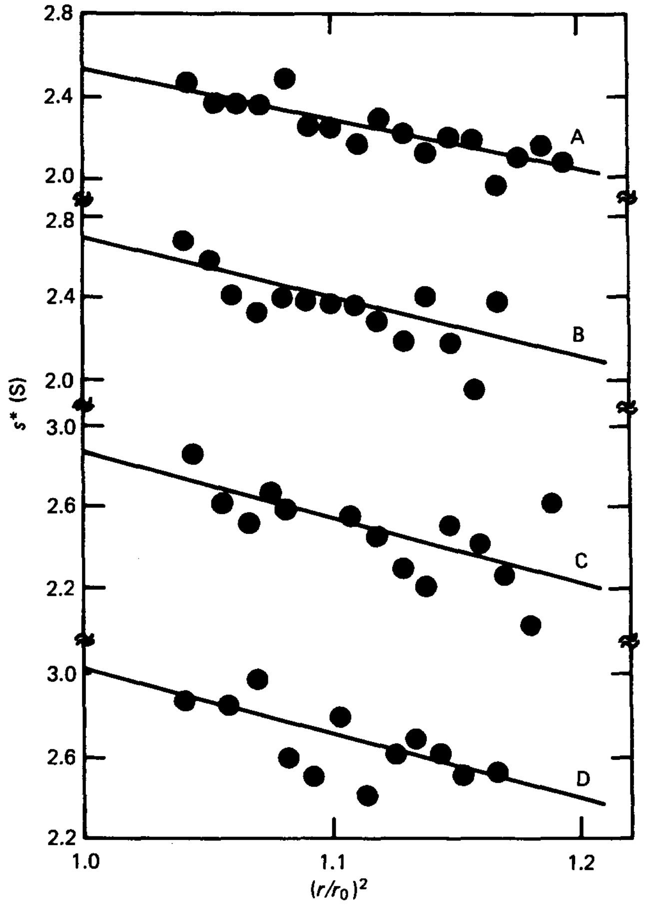

Figure 1 Elimination of the pressure effect on the sedimentation coefficient (in Svedberg units) according to equation (7). PDMS, sample 3, in BrCHX at 301 K. Lines A to D for initial concentration (g dl^{-1}): 1.264, 0.948, 0.632, 0.316, respectively

The course of sedimentation was followed using Philpot–Svensson optics. Photographs (20–30 exposures taken at different times for each concentration) were evaluated by a Zeiss two-dimensional travelling microscope. For the observed symmetric gradient curves the position of the boundary was taken as that of the maximum with a reproducibility better than 0.01 mm.

Since the density of PDMS is lower than that of BrCHX, the solute moved in the centripetal direction. Flotation of PDMS in this solvent strongly depends on the pressure change in the cell. The pressure effect was eliminated according to equation (7) (see below), i.e. by plotting $s^* \equiv \Delta \log r/(\omega^2 \Delta t)$ vs. $(r/r_0)^2 - 1$ and extrapolating to $(r/r_0)^2 - 1 = 0$. Here, r_0 and r are, respectively, the position of the boundary at the beginning (i.e. at the bottom of the cell) and at time t, and ω is the angular velocity. In this way, the sedimentation coefficient, s°_c, at unit pressure and concentration c was obtained. No correction for the acceleration period was needed, but the plot was very sensitive to a precise determination of the boundary position. An example of the extrapolation is presented in *Figure 1*.

To keep the pressure effect low and to meet the assumptions underlying this procedure (cf. 'Discussion'), measurements were always run with short columns (<5 mm) in the cell.

The sedimentation coefficients at unit pressure and zero concentration, s_0°, were obtained in the usual way, i.e. by extrapolating the plot of $1/s_c^\circ$ vs. c to zero concentration (*Figure 2*). The values of s_0° and k_s (coefficient of the concentration dependence of s_c°) for θ conditions are given in *Table 1*.

RESULTS AND DISCUSSION

Estimation of the M_w and s_0° values

Measurement of molecular weights (M_w) by light scattering in BrCHX revealed the presence of a small amount of high-molecular-weight particles. The angular dependences in Zimm plots were curved at low angles (*Figure 3*); as the curvature varied with the speed and/or number of cleaning operations (filtration), it seems that these particles can partly be separated by filtration.

The sedimentation diagrams did not indicate the presence of such particles but the quasielastic light scattering in BrCHX did. A typical example of a correlation curve is shown in *Figure 4*; a slow mode appeared in the range of longer relaxation times.

The high-molecular-weight particles can raise the M_w values by as much as 150% in some cases and make the determination of molecular weights in BrCHX unreliable, even though the second virial coefficient approaches zero (cf. *Figure 3* and *Figure 5*). Even an increased temperature (320 K) did not destroy them. Their effect on scattered light was the stronger the higher the molecular weight. The presence of high-molecular-weight particles in solutions of PDMS in BrCHX (less than 1%) is surprising, because previous studies of this system did not detect any anomaly[6,13]. The origin and structure of these particles is unknown.

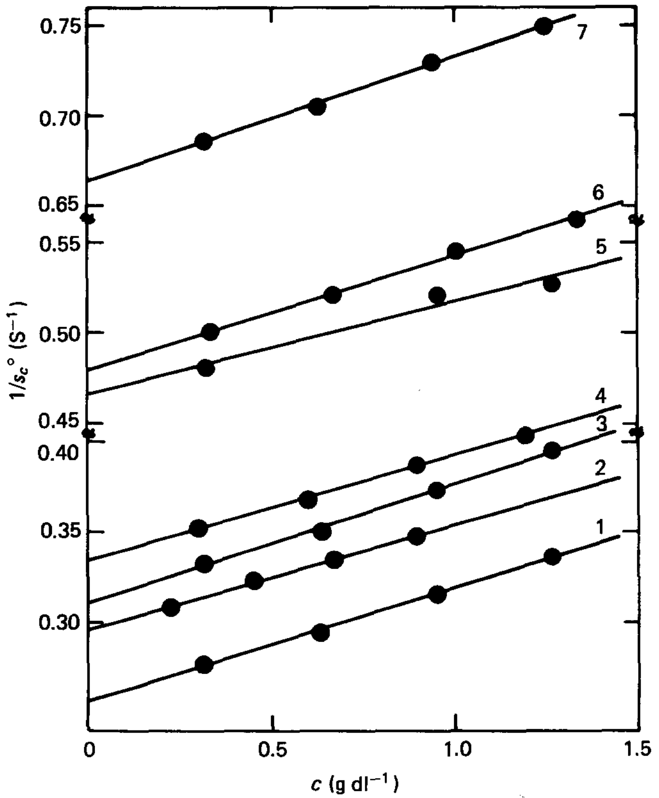

Figure 2 Concentration dependence of the sedimentation coefficients (in Svedberg units) of PDMS in BrCHX at 301 K. Lines denoted by code numbers of fractions (*Table* 1)

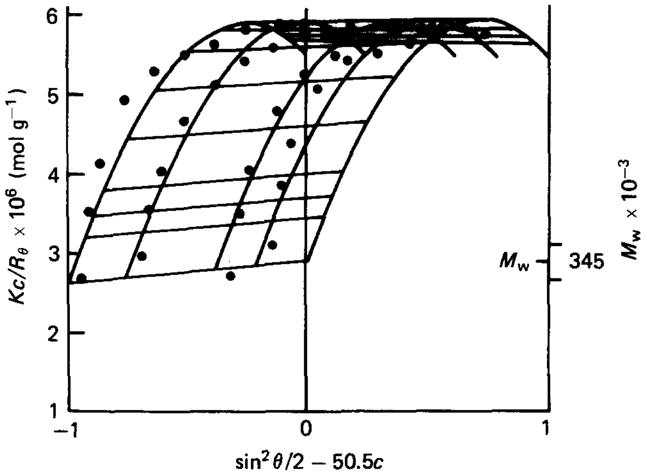

Figure 3 Zimm plot for sample 2 in BrCHX

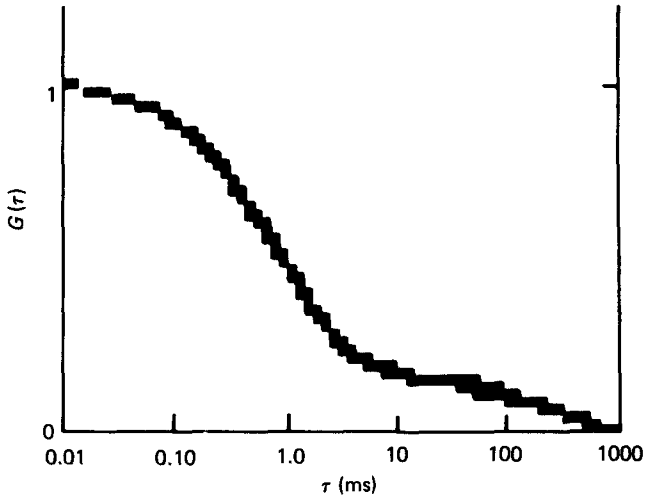

Figure 4 Correlation curve from QELS for sample 2 in BrCHX

Three fractions (2, 4 and 6) were chosen for the determination of M_w by light scattering in toluene (*Table 1*), which is a good solvent for PDMS. In this system, the Zimm plots were linear (*Figure 5*) even at the highest molecular weights, and the M_w values were lower than in bromocyclohexane. No high-molecular-weight component was detected in toluene by QELS and sedimentation. A disadvantage of this system is the high value of the second virial coefficient, which unfavourably affects the extrapolation to infinite dilution and, consequently, the accuracy of M_w values[14].

For the other fractions the viscosity-average molecular weight, M_η, was estimated by means of equation (1) with $K_{0,\eta}=\Phi_{0,\infty}(\langle R^2\rangle_0/M)^{3/2}=0.78\times10^{-3}\,\mathrm{dl\,g^{-1}}$. This is the arithmetic mean of the $[\eta]_\theta/M_w^{1/2}$ values calculated (with a standard deviation of $\pm0.04\times10^{-3}$) from reported data[6,7,13,15] for $M\geqslant10^5$. The $[\eta]_\theta/M_w^{1/2}$ values for our fractions 2, 4 and 6 agree fairly well with this value.

The main source of systematic errors in the sedimentation coefficients is their dependence on pressure in the ultracentrifuge cell. With the PDMS/BrCHX system, the pressure correction of the sedimentation coefficient s_c° is large (about 15% at $(r/r_0)^2$ as low as 1.1). Consequently, the sedimentation coefficients could not be evaluated from the time dependence of the logarithm of

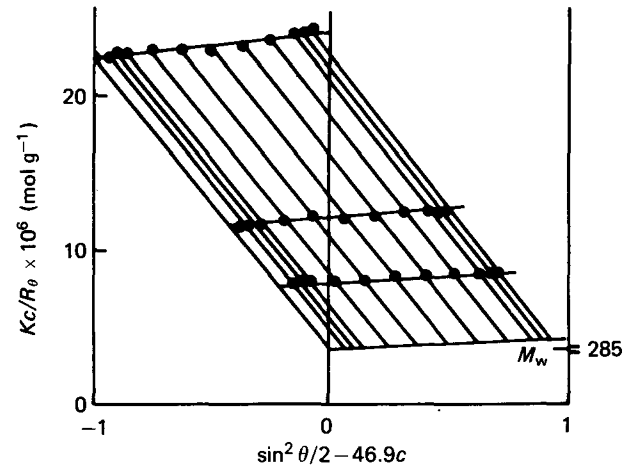

Figure 5 Zimm plot for sample 2 in toluene

position of the boundary, which was non-linear. Neither could the 'best fit method' be used (which, by extrapolation to meniscus, eliminates the pressure effect and simultaneously corrects for the acceleration period) because, at the beginning of the experiments, the boundary was at the bottom of the cell where the pressure effect was the largest.

The procedure used in the present paper (cf. 'Experimental') avoids these difficulties. It is based on a simplified form of the standard equation[16]

$$\frac{\mathrm{d}(\ln r)}{\mathrm{d}(\omega^2 t)} = \frac{s_0^\circ}{1 + k_s c (r_0/r)^2}\left\{1 - m\left(\frac{1+2k_s c}{1+k_s c}\right)\left[\left(\frac{r}{r_0}\right)^2 - 1\right]\right\} \quad (5)$$

where k_s is the coefficient of the concentration dependence of s_c°, and the coefficient $m = 0.5\gamma\omega^2 r_0 \rho_0^2$ is proportional to the parameter γ which includes the pressure effect on the solvent viscosity and density, and the polymer compressibility. If the concentration dependence of the sedimentation coefficient is expressed by the equation

$$s_c^\circ = s_0^\circ/(1 + k_s c) \quad (6)$$

and if differentials are replaced by differences, equation (5) can be simplified, for $(r/r_0)^2 < 1.2$, to

$$s^* = \frac{\Delta \ln r}{\omega^2 \Delta t} = s_c^\circ\left\{1 - m\left(\frac{1+2k_s c}{1+k_s c}\right)\left[\left(\frac{r}{r_0}\right)^2 - 1\right]\right\} \quad (7)$$

A plot of s^* vs. $(r/r_0)^2 - 1$ directly yields s_c°. An error introduced by the simplification is lower than 2%.

The reliability of estimation of s_c° was checked by the approximate constancy of the m values obtained from the slopes of plots based on equation (7) (*Figure 1*).

The concentration dependence of s_c° according to equation (6) was small, and the values of $k_{s,\theta}/[\eta]_\theta = 0.55 \pm 0.08$ correspond to θ conditions. Similarly, the Huggins coefficients, $k_{\mathrm{H},\theta} \simeq 0.50 \pm 0.05$, were very close to the values usually found for θ systems (*Table 1*).

The evaluation of s_0° described here differs from that used by Haug and Meyerhoff[6]. The pressure correction in their paper was calculated according to the empirical equation $s_c = s_c^\circ(1 + 1.3 \times 10^{-2} p)$ valid for pressures $p < 30$ atm. The positive sign of the pressure term is obviously a misprint but its magnitude is larger than that estimated from our data by nearly an order of magnitude. The sedimentation coefficient is said to be independent of concentration, which is at variance with our finding (*Figure 2*).

Analysis of hydrodynamic data

The most direct way to check the validity of equation (2) would be a plot of log s_0° vs. log M. Since, however, the intrinsic viscosity can usually be measured with a better accuracy than the molecular weight, we plot logarithmically s_0° vs. $[\eta]$, The slope of this plot should be unity under θ conditions and lower than unity for good solvent systems[17]. It is more sensitive to the excluded-volume effects than are the slopes of the logarithmic plots of s_0° vs. M or $[\eta]$ vs. M. For PDMS in BrCHX at 301 K (*Figure 6*), the correlation is tight and the slope $a_{s,\eta} = 0.98$ (least-squares value) is practically identical with that predicted for a system without excluded-volume effect (θ conditions).

The validity of equations (1) and (2) can also be checked by calculating the values of $[\eta]_\theta/s_{0,\theta}^\circ$ which, according to the equation[18]

$$[\eta]_\theta/s_{0,\theta}^\circ = [N_{\mathrm{A}}\eta_0/(1 - \bar{v}\rho_0)](\Phi_{0,\infty}P_{0,\infty})(\langle R^2\rangle_0/M)_\infty^2 \quad (8)$$

should be invariant with respect to molecular weight. This check is equivalent to the plot in *Figure 6*. The values of $[\eta]_\theta/s_{0,\theta}^\circ$ for PDMS in BrCHX at 301 K based on data in *Table 1* are constant over the range $4 \times 10^4 < M < 25 \times 10^4$. Their arithmetic mean is 0.111 $(\pm 0.001) \times 10^{13}$.

By means of equation (8) we estimate the value of $(\langle R^2\rangle_0/M)_\infty$ (Ref. 18). Because $[\eta]_\theta/s_{0,\theta}^\circ$ is proportional to $(\langle R^2\rangle_0/M)_\infty^2$, an error in the result is smaller than an error in measured quantities ($[\eta]_\theta$, $s_{0,\theta}^\circ$) or constants (η_0, $1 - \bar{v}\rho_0$, $\Phi_{0,\infty}P_{0,\infty}$). This is particularly important because, though the empirical values of $\Phi_{0,\infty} \times 10^{-21} = 2.5$–$2.6$ g^{-1} are generally accepted[1,19] as the best estimates, the value of $P_{0,\infty}$ is, at present, an object of vivid discussion.

Among the theoretical values (5.11, 5.20[20,21], 6.0[22]) only the last estimate lies within the broad interval of

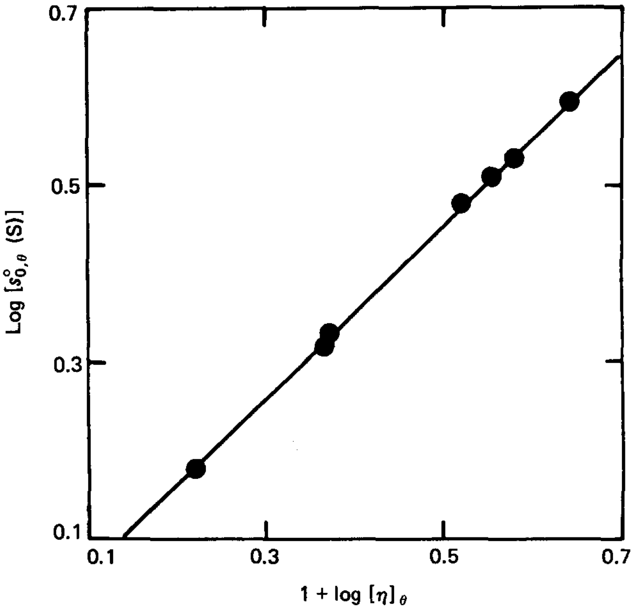

Figure 6 Logarithmic plot of $s_{0,\theta}^\circ$ vs. $[\eta]_\theta$ for PDMS in BrCHX at 301 K

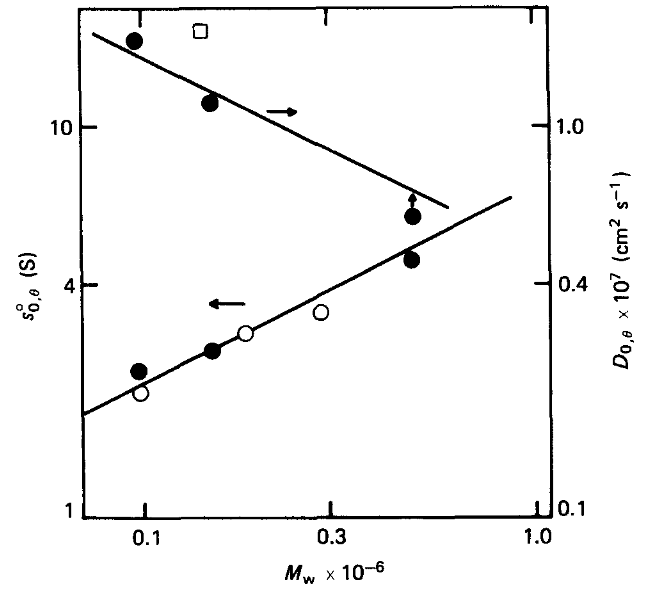

Figure 7 Logarithmic plot of $s^{\circ}_{0,\theta}$ and $D_{0,\theta}$ vs. M_w for PDMS in BrCHX at 301 K. Data points: ○, this work (*Table 1*); ●, ref. 6; □, ref. 4. Lines calculated as described in text

empirical values (5.8–6.7)[23–27]. By combining, e.g. $\Phi_{0,\infty} = 2.5 \times 10^{21}$ with the limits of this interval, we obtain $14.5 \leqslant \Phi_{0,\infty} P_{0,\infty} \times 10^{-21} \leqslant 16.7$. Owing to the form of equation (8), the large uncertainty in $\Phi_{0,\infty} P_{0,\infty}$ fortunately reduces to an inaccuracy of about 7% in $(\langle R^2 \rangle_0/M)_\infty$.

The value of $(\langle R^2 \rangle_0/M)_\infty$ for PDMS calculated according to equation (8) with $\Phi_{0,\infty} = 2.5 \times 10^{21}$ g^{-1} and $P_{0,\infty} = 6.2$ (centre of the above range of empirical values) is 0.47×10^{-16} cm^2 and is identical with that estimated by Zilliox *et al.*[15] from the intrinsic viscosity and from the radii of gyration (after correction for polydispersity).

Let us look at the molecular weight dependences of the sedimentation and diffusion coefficients represented in *Figure 7* in logarithmic scales. Straight lines were calculated according to equations (1) and (8) with $K_{0,\infty} = 0.78 \times 10^{-3}$ and $[\eta]_\theta / s^{\circ}_{0,\theta} = 0.111 \times 10^{13}$. Their slopes are equal to 1/2 and −1/2, respectively. Deviations of the experimental points from lines do not exceed the limits of error of correlated quantities.

Possible errors in M_w (in general) and in the values from ref. 6 have been discussed above, and significant inaccuracy in the diffusion coefficients can be expected because of their low absolute values. The magnitude of errors in hydrodynamic quantities is seen from the values of the friction coefficient computed from the diffusion or sedimentation data for the same fraction[6]; they differ by as much as 10% (e.g. for $M_w = 4.9 \times 10^5$, $[f]_\theta \times 10^5 = 3.34$ from sedimentation and 3.70 from diffusion). Irrespective of the excluded-volume effect they should be identical.

The only value in *Figure 7* which deviates strongly from the line and from the other experimental data is the diffusion coefficient measured[4] by QELS for $M_w = 148 \times 10^3$. The reason for this deviation is unknown to us.

CONCLUSIONS

The plot of log $s^{\circ}_{0,\theta}$ vs. log $[\eta]_\theta$ in *Figure 6*, the constancy of the $[\eta]_\theta / s^{\circ}_{0,\theta}$ values, and the agreement of the $(\langle R^2 \rangle_0/M)_\infty$ values estimated by different methods lead us to a conclusion that, similarly to other flexible chain polymers, the translational friction properties of PDMS (at $M \gtrsim 40 \times 10^3$) under θ conditions do not display excluded-volume effects and can be described by equation (2). Deviations found previously[2,3,4] can be assigned to experimental errors.

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