eration. This factor was not considered in the choice of functional polymer for binding of hydrazine and the subject of stabilization will not be dealt with in this paper. However, the fact that poly(acrylic acid) is effective in stabilizing hydrophobic sols, such as Se in water, is understandable in terms of the conventional conception of steric and charge stabilization.[14,15]

Summary

Stable colloidal dispersions of amorphous selenium can be simply prepared with the agency of hydrazonium salts of polyacids. The formation of these dispersions has been rationalized in terms of localization of the selenium-forming reaction in the domain of individual macromolecules. The procedure, which we have termed locus control, allows for the preparation of nearly monodisperse selenium sols in the range of 1000–2000 Å. We believe that this is the first instance in which the utility of polymer-bound reagents in the preparation of colloidal sols has been recognized.

Acknowledgment. We thank Dr. W. H. H. Gunther for his contribution in devising chemistry through which locus control could be applied to the preparation of colloidal dispersions of selenium. We also express our appreciation to K. Johnson for his efforts in obtaining electron micrographs on these dispersions.

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Friction Coefficient of Polymer Molecules in Dilute Solution near the Θ Point. 1. A Rapid Method for Determining Small Differences in Sedimentation Coefficients: Polystyrene in Cyclohexane

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ABSTRACT: A rapid and accurate method for determining small differences in sedimentation coefficients in the analytical ultracentrifuge is described. The method compares distances traveled by two solvent–solution boundaries in equal periods of time under slightly different conditions of concentration or temperature. Narrow-distribution polystyrenes in the Θ solvent cyclohexane are used for illustration of the method. The following results are obtained: The coefficient of concentration dependence of the reciprocal value of the sedimentation coefficient is $(k_s)_\Theta = (4.1 \pm 0.2) \times 10^{13} s^0 = (0.062 \pm 0.003) M^{1/2}$ mL/g. This value is definitely smaller than the intrinsic viscosity, in contradiction to a theoretical result by Freed. The temperature coefficient of the sedimentation coefficient at infinite dilution is $(\mathrm{d} \ln s^0/\mathrm{d}T)_\Theta = (1.85 \pm 0.03) \times 10^{-2} - (0.87 \mp 0.04) \times 10^{-5} M^{1/2}$ deg^{-1}. For $M \geq 10^5$ the temperature dependence of k_s can be represented by $(\mathrm{d}k_s/\mathrm{d}T)_\Theta = (0.3 \pm 0.1) + (0.87 \mp 0.02) \times 10^{-5} M$ mL g^{-1} deg^{-1}. In addition we found $s_\Theta{}^0 = (1.51 \pm 0.02) \times 10^{-15} M^{1/2}$ s in accordance with literature data. A comparative discussion is given of the temperature dependence of the expansion factors for differently defined radii of the polymer molecule. Doubts are raised with respect to the reliability of recent first-order perturbation theories for the intrinsic viscosity. The concentration dependence of s will be discussed in a subsequent paper.

Introduction

In the past different results have been obtained with respect to the vanishing or nonvanishing of the concentration dependence of the sedimentation coefficient of random-coil polymers in dilute Θ solutions. We refer to the coefficient $(k_s)_\Theta$ defined by the relation

$$s(c) = s(0)/\{1 + (k_s)_\Theta c\} \qquad (T = \Theta) \qquad (1)$$

The early conclusion reached by Cantow[1] about a vanishing concentration dependence for polystyrene (PS) in cyclohexane (CH) at 35 °C was disproved by preponderant experimental evidence in later years.[2-9] Haug and Meyerhoff[10] reported that $(k_s)_\Theta$ is zero for the Θ system poly(dimethylsiloxane) in bromocyclohexane at 28 °C. Llopis et al.[11] did the same with respect to poly(ethyl acrylate) in 1-propanol at 28 °C. Nonvanishing concentration effects were reported for poly(methyl methacrylate) in *n*-butyl chloride at 35 °C[7] and poly(α-methylstyrene) (PαMS) in CH at 38.2[9] and 39 °C.[12]

Contradictory results were also reached in the theory: Yamakawa[13] ($(k_s)_\Theta = 0$) vs. Pyun and Fixman.[14] Recently (1976) a quite different conclusion was reached by Freed,[15] who claimed that $(k_s)_\Theta$ is equal to the intrinsic viscosity $[\eta]_\Theta$. Experimental data by Kotera and co-workers[9] were

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quoted in support of this result.

Data in the literature resulted from the comparison of sedimentation coefficients established in several centrifugations of solutions of different concentration.

The coefficient $(k_s)_\Theta$, however, can be evaluated from a direct comparison of boundary translations made in equal periods of time. Thus, time can be eliminated from the calculations. This diminishes desk work and, in addition, dispels the zero-time problem.

In the following a differential method is described, in which the calculation of sedimentation coefficients is omitted. The method will be demonstrated by determining both the concentration and temperature dependence of the sedimentation coefficient of PS in CH at the Θ temperature.

A Differential Method for Determination of the Coefficient of Concentration Dependence of the Sedimentation Coefficient

We consider the sedimentation of a narrow-distribution polymer in dilute solution in the standard ultracentrifuge cell. The solution is homogeneous at $t = t_0$.

The differential equation and initial condition for the boundary velocity are

$$\mathrm{d}r/\mathrm{d}t = \omega^2 r s(c, p) \qquad (r = r_0, \quad t = t_0) \tag{2}$$

r is the distance of the boundary to the axis of rotation and r_0 is that of the meniscus, ω is the angular speed of the rotor, and $s(c, p)$ is the sedimentation coefficient of the solute, which is dependent on the concentration (c) and pressure (p). Since at high rotor speeds a strong pressure gradient develops and its effect on the sedimentation velocity in organic solvents usually is considerable, we shall include this effect in the equations.

Up to values for $k_s c$ and μp about 0.25 the following relationship holds good:

$$s(c, p) = s_p{}^c = s_0{}^0/\{(1 + k_s c)(1 + \mu p)\} \tag{3}$$

The hydrostatic pressure at the position of the boundary is given by

$$p = \tfrac{1}{2}\rho_1 \omega^2 (r^2 - r_0{}^2) \tag{4}$$

Here ρ_1 is the solvent density.

Substitution of (4) in (3) and (3) in (2) and use of the dimensionless symbols

$$\begin{array}{lll} \xi \equiv (r^2/r_0{}^2) - 1 & \tau \equiv 2\omega^2 s_0{}^0 t & \Theta \equiv c/c_0 \\ \gamma \equiv k_s c_0 & m \equiv \tfrac{1}{2}\mu\rho_1\omega^2 r_0{}^2 & \end{array} \tag{5}$$

transforms eq 2 into

$$\frac{\mathrm{d}\xi}{\mathrm{d}\tau} = \frac{1 + \xi}{\{1 + \gamma\Theta(\xi)\}(1 + m\xi)} \qquad (\xi = 0, \quad \tau = 0) \tag{6}$$

We next consider the boundary velocity equations for two solutions of the same polymer but of different initial concentrations $(c_1)_0$ and $(c_2)_0$

$$\frac{\mathrm{d}\xi_i}{\mathrm{d}\tau} = \frac{1 + \xi_i}{\{1 + \gamma_i\Theta_i(\xi_i)\}(1 + m\xi_i)} \tag{7}$$
$$(\xi_i = 0, \quad \tau = 0; \quad i = 1, 2)$$

Here $\xi_i \equiv \{r_i{}^2/(r_i)_0{}^2 - 1\}$ and $\gamma_i \equiv k_s(c_i)_0$. In the coefficient m a small difference between $(r_1)_0{}^2$ and $(r_2)_0{}^2$ will be neglected.

Eliminating the time, we obtain

$$\frac{\mathrm{d}\xi_2}{\mathrm{d}\xi_1} = \frac{(1 + \xi_2)(1 + \gamma_1\Theta_1)(1 + m\xi_1)}{(1 + \xi_1)(1 + \gamma_2\Theta_2)(1 + m\xi_2)} \tag{8}$$
$$(\xi_1 = 0, \quad \xi_2 = 0)$$

Equation 8 can be integrated, after Θ_i has been expressed in terms of ξ_i. A close approximation for Θ_i is

$$\Theta_i = (1 + m\xi_i)/(1 + \xi_i) \qquad (i = 1, 2) \tag{9}$$

It is proven in the Appendix that the first neglected term in the right-hand member of (9) is of the order of magnitude $\gamma_i m \xi_i{}^2$.

Equation 8 with substitution of (9) can be integrated by means of a power series. For ξ_2 as a function of ξ_1 the result is

$$\xi_2 = \frac{1 + \gamma_1}{1 + \gamma_2}\xi_1 - \frac{(1 - m)(\gamma_2 - \gamma_1)(\gamma_1 + \gamma_2 + 2\gamma_1\gamma_2)}{2(1 + \gamma_2)^3}\xi_1{}^2 + \mathcal{O}(\xi_1{}^3) \tag{10}$$

Since the significance of the linear coefficient in (10) lies in its difference with unity, a more efficient arrangement is

$$\xi_1 - \xi_2 = \frac{\gamma_2 - \gamma_1}{1 + \gamma_2}\xi_1 + \frac{(1 - m)(\gamma_2 - \gamma_1)(\gamma_1 + \gamma_2 + 2\gamma_1\gamma_2)}{2(1 + \gamma_2)^3}\xi_1{}^2 + \mathcal{O}(\xi_1{}^3) \tag{11}$$

where it is assumed that $(c_1)_0 < (c_2)_0$, so that in general $\xi_1 > \xi_2$.

If Q is the initial slope of a plot of $\xi_1 - \xi_2$ vs. ξ_1, the parameter k_s follows from

$$k_s = Q/[(c_2)_0(1 - Q) - (c_1)_0] \tag{12}$$

The curvature of the plot is of the magnitude $(1 - m)\gamma_2{}^2$, so a substantial pressure effect $(m\uparrow 1)$ will favor a linear variation of ξ_2 with ξ_1.

Concentrations should differ by a factor of 3 or 4. One of the cells should be provided with a wedge window to separate the gradient patterns on the photographic plate.

Thus, in addition to the elimination of t, the following advantages are realized: (1) determination of k_s in a single centrifugation, (2) a force field and temperature which are strictly equal at any moment, and (3) without special care ξ_1 and ξ_2 refer to the same experimental time.

Since only two concentrations are used, a duplicate experiment is advisable. Pressure dependence of k_s will not invalidate the method because it will not manifest itself until the coefficient of the squared term.

Temperature Coefficient of the Sedimentation Coefficient

For determining a temperature coefficient of the sedimentation coefficient a solution of given concentration is centrifuged twice at different temperatures.

We will deduce the equation which underlies the extrapolation yielding the required coefficient.

In the expression for $s_p{}^c$ (eq 3) both $s_0{}^0$ and k_s are dependent on the temperature. We neglect a small variation in μ because we know from eq 10 that the pressure effect does not appear in the term linear in ξ_1. The differential equation (7) and the initial value may then be written

$$\frac{1}{2\omega^2 s_i{}^0(T_i)}\frac{\mathrm{d}\xi_i}{\mathrm{d}\tau} = \frac{1 + \xi_i}{\{1 + \gamma_i(T_i)\Theta_i(\xi_i)\}(1 + m\xi_i)} \tag{13}$$
$$(\xi_i = 0, \quad \tau = 0; \quad i = 1, 2)$$

Here $\gamma_i = k_s(T_i)c_0$, c_0 being the same for the two solutions. Dividing the second equation by the first eliminates time

$$\frac{\mathrm{d}\xi_2}{\mathrm{d}\xi_1} = \frac{s_2{}^0\{1 + \gamma_1\Theta_1(\xi_1)\}(1 + \xi_2)(1 + m\xi_1)}{s_1{}^0\{1 + \gamma_2\Theta_2(\xi_2)\}(1 + \xi_1)(1 + m\xi_2)} \tag{14}$$
$$(\xi_2 = 0, \quad \xi_1 = 0)$$

Table I
Specification of Polystyrenes, Sedimentation Coefficients at Infinite Dilution, and Coefficients for the Concentration Dependence of s Obtained by Two Methods[a]

$10^{-3} \times \overline{M}_w$	batch no. of manuf	$\overline{M}_w/\overline{M}_n$	$10^{13} s_\Theta{}^\circ$, s	$(k_s)_\Theta$, mL/g from $1/s$ vs. c	$(k_s)_\Theta$, mL/g from ξ_1 vs. ξ_2
97	4a	$\leqslant$1.06	4.64 ± 0.04	19 ± 1.5	17 ± 1
160	1a	$\leqslant$1.06	5.93 ± 0.03	21.5 ± 1	23.5 ± 1
190	1c	$\leqslant$1.06	6.44 ± 0.03	26 ± 1	26 ± 1
410	3a	$\leqslant$1.06	9.68 ± 0.08	38 ± 4	40 ± 2
860	6a	$\leqslant$1.15	14.05 ± 0.08	58 ± 4	57 ± 4
1800		$\leqslant$1.20	-	-	

[a] Data for cyclohexane solutions and $T = 34.5$ °C.

After substituting for Θ_i from (9), (14) is integrated by again using a power series. For ξ_2 as a function of ξ_1 one obtains

$$\xi_2 = \frac{(1+\gamma_1)s_2{}^0}{(1+\gamma_2)s_1{}^0}\xi_1 + \frac{(1-m)s_2{}^0\{(1+\gamma_1)^2(1+2\gamma_2)s_2{}^0 - (1+\gamma_2)^2(1+2\gamma_1)s_1{}^0\}}{2(1+\gamma_2)^3(s_1{}^0)^2}\xi_1{}^2 + \mathcal{O}(\xi_1{}^3) \quad (15)$$

As before, a more efficient procedure will be the plotting of $\xi_2 - \xi_1$ vs. ξ_1. Designating the initial slope of such a plot as R, we have

$$R = \frac{(1+\gamma_1)s_2{}^0}{(1+\gamma_2)s_1{}^0} - 1 \equiv \frac{s(c_0, T_2)}{s(c_0, T_1)} - 1 \quad (16)$$

Since for determining $\Delta \ln s$ the average value of s should be in the denominator, we write

$$\frac{s(c_0, T_2) - s(c_0, T_1)}{s(c_0, T_2) + s(c_0, T_1)} = \frac{R}{2+R} \quad (17)$$

Let one experiment be made at $T_1 = \Theta - \Delta T/2$ and the other at $T_2 = \Theta + \Delta T/2$. Expanding the numerator and denominator of the left-hand member of (17) in a Taylor series, we obtain

$$\frac{s\left(c_0, \Theta + \dfrac{\Delta T}{2}\right) - s\left(c_0, \Theta - \dfrac{\Delta T}{2}\right)}{s\left(c_0, \Theta + \dfrac{\Delta T}{2}\right) + s\left(c_0, \Theta - \dfrac{\Delta T}{2}\right)} \Longrightarrow \frac{\Delta T}{2}\,\frac{\left(\dfrac{\mathrm{d}s}{\mathrm{d}T}\right)_\Theta + \dfrac{2}{3!}\left(\dfrac{\mathrm{d}^3 s}{\mathrm{d}T^3}\right)_\Theta\left(\dfrac{\Delta T}{2}\right)^2 + \mathcal{O}\left(\dfrac{\Delta T}{4}\right)^4}{s(c_0, \Theta) + \dfrac{1}{2!}\left(\dfrac{\mathrm{d}^2 s}{\mathrm{d}T^2}\right)_\Theta\left(\dfrac{\Delta T}{2}\right)^2 + \mathcal{O}\left(\dfrac{\Delta T}{4}\right)^4} \quad (18)$$

A linear variation of s with T in the interval $T_2 - T_1$ is not required because in the numerator the second derivative of s with respect to T has vanished. Hence the left-hand member may be equated to the ratio of the first terms to the right over a range of several degrees. We thus have

$$\left(\frac{\Delta \ln s}{\Delta T}\right)_\Theta = \frac{2R}{\Delta T(R+2)} \quad (19)$$

which is our final equation.

Because $\gamma_1, \gamma_2 \ll 1$, the coefficient of the squared term in eq 15 is of the order of magnitude $^1/_2(1-m)\Delta \ln s^0$. Once more a large pressure effect will suppress the nonlinearity in the variation of ξ_2 with ξ_1.

Since boundary translations that will be compared are not obtained in a single centrifugation, not only the stationary speed but also the acceleration should be equal for the two runs.

Experiments

Narrow-distribution polystyrenes were obtained from Pressure Chemical Co. Specifications are in Table I. $\overline{M}_w$ (from light scattering) and $\overline{M}_w/\overline{M}_n$ are from the manufacturer except for batch no. 1c. On the grounds of our results for $s_\Theta{}^0$, $[\eta]$, and elution volume at GPC, a value $\overline{M}_w = 2 \times 10^5$ was considered as too large. For the sample of high $\overline{M}_w$ the low-molecular-weight tail was removed by means of GPC. From $s_\Theta{}^0$ in cyclohexane, $\overline{M}_w$ of the retained portion was estimated as 1.8×10^6.

Cyclohexane of analytical reagent grade was supplied by Merck. Its nominal water content was 0.01% and it was used without further drying.

Aluminum cell centerpieces of 6- or 12-mm thickness were used, depending on concentration and molecular weight. The windows toward the light source were sapphire and those toward the camera were quartz.

In the study of k_s, the concentration ratio of solutions that were simultaneously centrifuged was 1:3 or 1:4. The cell containing the solution of lower concentration, which had a lower gradient peak and a more rapidly moving boundary, was left with a slightly larger air bubble at filling and had a 1° negative wedge window. In this way the schlieren patterns of the two gradient peaks remained well separated.

For comparison $(k_s)_\Theta$ was also determined in the conventional way by establishing s as a function of c. A careful reading of the steep parts of the schlieren gradient pictures was carried out. Details will be given elsewhere.

Two solutions of different concentration were also centrifuged in runs for determining the temperature coefficient, first at 3 °C below Θ and then, after redissolution of the sediment and homogenization of the solution, at 3 °C above.

A Spinco E analytical ultracentrifuge was used with a rotor temperature indication and control unit. The operating speed was 59 780 rpm. For runs at different temperatures but equal concentration, for which the boundary translations had to be compared, care was taken that once 14 A was applied to the drive, equal rotor speeds were attained in equal time intervals. At corresponding times six or more exposures were taken at equal time intervals. The boundary positions were chosen in the range $0 < \xi \lesssim 0.3$.

The adiabatic temperature decrease of about 0.8 °C was offset by setting the initial temperature 0.6 °C above the equilibrium temperature of 34.5 ± 0.1 °C. Even though the uncertainty in the absolute value is 0.1 °C, the error in the adjusted interval of 6 °C was certainly smaller.

The camera lens was adjusted following the instructions given by Svensson.[16] A plane situated at two-thirds of the centerpiece's thickness in the solvent-filled cell, measured from the plane of light entrance, was made the conjugate image plane of the photographic plate.

Two or three pairs of points on the steep sections of the schlieren gradient curves were measured. Each pair was on a line parallel to the base line. An average of the distances of these points from the meniscus was taken as the distance of the equivalent boundary point.

The kinematic viscosities of cyclohexane and aqua bidest. were measured with a Hewlett-Packard Auto-Viscometer system. The viscometer was of the Ubbelohde type. Corrections for kinetic energy were taken from a table furnished by the manufacturer (Schott).

The expansion coefficient of cyclohexane was measured in duplicate by using pycnometers of the capillary type.

Results and Discussion

Concentration Dependence of s at the Θ Temperature. The linear variation of $1/s$ with c for a wide range of $k_s c$ is well-known and need not be demonstrated again. Least-squares methods were used to calculate values for $s_\Theta{}^0$ and $(k_s)_\Theta$ (Table I, columns 4 and 5). Figure 1 serves as a check on the consistency of $s_\Theta{}^0$ and $\overline{M}_w{}^{1/2}$.

The small curvature in the plots of $\xi_1 - \xi_2$ vs. ξ_1 for the differential method is shown in Figure 2. (With $\mu = 1.5$

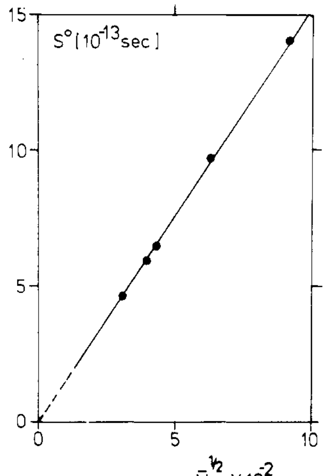

Figure 1. Check of compatibility of s_Θ^0 and $\bar{M}_w^{1/2}$. Polystyrene–cyclohexane, $T = \Theta = 34.5$ °C ($s_\Theta^0 = 1.51 \times 10^{-15}\bar{M}_w^{1/2}$).

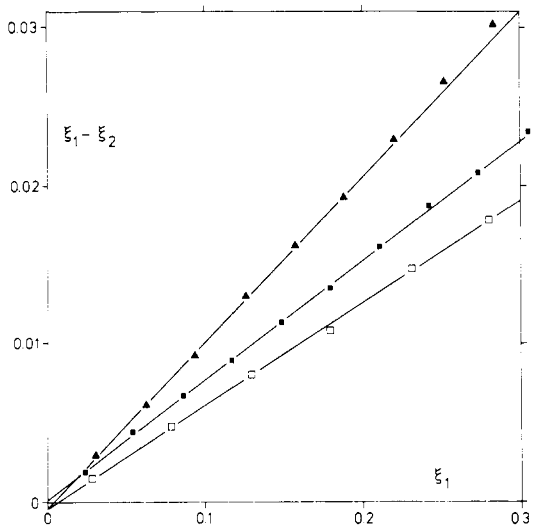

Figure 2. Demonstration of small curvature in plots of $\xi_1 - \xi_2$ vs. ξ_1 at a large pressure effect. (□) $M = 16 \times 10^4$ (concentrations 0.186 and 0.560 w/w %); (■) $M = 41 \times 10^4$ (0.145 and 0.419 w/w %); (▲) $M = 86 \times 10^4$ (0.125 and 0.427 w/w %). PS–CH, 34.5 °C. Rotor speed 59 780 rpm.

$\times 10^{-9}$ cm²/dyn, the estimated value of m (eq 5 and 11) is 0.83.) Values for $(k_s)_\Theta$ are the average of two experiments (Table I, column 6).

The results of the two methods have been plotted vs. s_Θ^0 and $\bar{M}_w^{1/2}$ in Figure 3 together with data published by other authors. For the source material see the caption.

The results agree very well and indicate a proportional relation between $(k_s)_\Theta$ and s_Θ^0 in accordance with the Pyun–Fixman theory, namely

$$(k_s)_\Theta = k_\Theta^* s_\Theta^0 \text{ mL/g}$$

$$k_\Theta^* = (4.1 \pm 0.2) \times 10^{13} \text{ mL g}^{-1} \text{ s}^{-1} \qquad (20)$$

When the exponent α in the familiar relation $s^0 = KM^\alpha$ is given the value 0.5, columns 1 and 4 of Table I are best correlated by $s_\Theta^0 = 1.51 \times 10^{-15}\bar{M}_w^{1/2}$ s. A coefficient $K = 1.50 \times 10^{-15}$ was found by Cowie and Bywater,[17] who studied seven molecular weights. Kotera et al.[9] reached 1.52×10^{-15} from 13 data (s_Θ^0, $\bar{M}_w$) taken from six papers.

We thus may write

$$(k_s)_\Theta = \mathbf{k}_\Theta M^{1/2} \text{ mL/g}$$

$$\mathbf{k}_\Theta = 0.062 \pm 0.003 \text{ mL g}^{-3/2} \text{ mol}^{-1/2} \qquad (21)$$

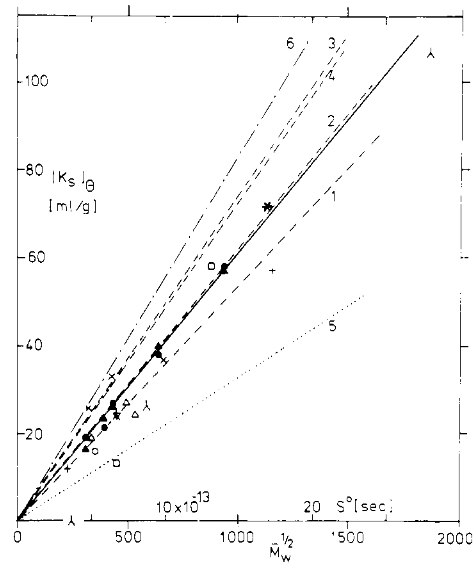

Figure 3. Variation of $(k_s)_\Theta$ with s_Θ^0 and $M^{1/2}$ for polystyrene in cyclohexane. $\Theta = 34.5$ °C. (●) This work, from $1/s$ vs. c; (▲) this work, from ξ_1 vs. ξ_2; (□) Wales and Rehfeld;[2] (△) Billick;[3] (▽) Billick;[4] (⅄) Homma et al.;[5] (○) Blair;[6] (*) Closs et al.;[7] (+) Petrus et al.;[8] (×) Kotera et al.[9] The solid line is drawn to fit the present data. Broken lines indicate theoretical results: 1, 2, and 3 by Pyun and Fixman;[14] 4, modification by Mulderije;[19] 5, theory by Imai;[21] 6, theory by Freed[15] ($(k_s)_\Theta = [\eta]_\Theta$).

Dashed lines 1, 2, and 3 (Figure 3) represent theoretical results by Pyun and Fixman.

In this theory the model of the interpenetrable friction equivalent sphere is used, and the concentration is expressed in the volume fraction of spheres Φ. A single numerical result was not reached because the authors were obliged to approximate the friction coefficient of two equivalent spheres in partial overlap by means of the friction coefficient of an ellipsoid. For this they offered a choice of three sizes. Values for $(k_\phi)_\Theta$ were recalculated by us and turned out to be slightly different: 2.06, 2.37, and 2.85 rather than 2.23, 2.60, and 2.96.[19] For translating them into $\mathbf{k}_\Theta$ by means of the relation[14]

$$(\mathbf{k}_\Theta)_{\text{theor}} = (k_\phi)_\Theta (6\pi N_A)^{-1} \left(\frac{1 - \bar{V}_p \rho_1}{3\eta_1 K} \right)^3 \qquad (T = \Theta) \quad (22)$$

we used the following numerical values: $\rho_1 = 0.766$ g/mL, $\bar{V}_p = 0.934$ mL/g[18] and K is as given above; the viscosity η_1 of cyclohexane at 34.5 °C was found to be 0.768 cP, with 0.7267 for aqua bidest. as a reference.[20]

Line 4 (Figure 3) gives the result for a modification of the Pyun–Fixman theory. This will be treated in a subsequent paper.[19]

We also mention an expression for k_s by Imai.[21] This author tried to improve on Yamakawa's theory,[13] which predicted $(k_s)_\Theta = 0$. Imai's equation is

$$k_s = \frac{N_A}{8\pi^{3/2}} \frac{nb^2}{M}[f] \qquad (23)$$

n and b are the number and length of the segments of the statistically equivalent chain and $[f]$ is the intrinsic friction coefficient ($= f/\eta_1$).

Substituting $\langle l_0^2 \rangle$ for nb^2 along with Kirkwood and Riseman's[22] relation

$$[f]_\Theta = P(\langle l_0^2 \rangle)^{1/2}$$

$$P = \tfrac{1}{2}(3\pi/2)^{3/2} \qquad (24)$$

we have

$$(k_s)_\Theta = \frac{N_A}{16}\left(\frac{3}{2}\right)^{3/2}\left(\frac{\langle l_0^2\rangle}{M}\right)^{3/2} M^{1/2} \qquad (25)$$

When for the unperturbed dimensions of PS a value is taken from Cowie and Bywater[17] $[(\langle l_0^2\rangle/M)^{1/2} = (7.8 \pm 0.2) \times 10^{-9}$ cm from light scattering by narrow-distribution polystyrenes], $(k_s)_\Theta$ is found to be $(0.033 \pm 0.002)M^{1/2}$ mL/g, which is shown by line 5 (Figure 3).

Finally, we mention Freed,[15] who arrived at $(k_s)_\Theta = [\eta]_\Theta$ ($=0.084M^{1/2}$ mL/g, line 6 (Figure 3)). This result is rather different from that by other authors. Freed claimed that it is confirmed by experimental data for $[\eta]_\Theta$ and $(k_s)_\Theta$ for PαMS in CH at 38.2 °C and for PS in CH at 35 °C by Kotera et al.[9] The random error in the data for $(k_s)_\Theta$ is rather large, however, so we will consult conclusions reached by other authors as well.

Values for PαMS–CH found by Abe et al.[12] are markedly different. These authors concluded $(k_s)_\Theta = 0.062M^{1/2}$ mL/g and $[\eta]_\Theta = 0.076M^{1/2}$ mL/g ($\Theta = 38.6$ °C).

A significant difference between $(k_s)_\Theta$ and $[\eta]_\Theta$ for PαMS–CH at 39 °C is not discerned in data by Noda et al.[23] It is suggested by these authors, however, that their working temperature was somewhat above Θ. This is important because the rate of increase of k_s with temperature in the vicinity of the Θ point is much larger than that of $[\eta]$.[9] The former arises from both the increased mutual repulsion of molecules, which gives the major contribution, and coil expansion,[20] whereas the latter increases only through coil expansion. It should also be noted that the Θ point for PαMS varies with its tacticity.

Recently (1977) Noda et al.[24] studied once more the friction coefficient and its concentration dependence for PαMS in a few solvents. This time the Θ temperature in CH was stated to be 34.5 °C. From tabulated data we derived $(k_s)_\Theta = (0.056 \pm 0.005)\bar{M}_w^{1/2}$ mL/g. This value is even smaller than Abe's.

In view of these facts there can be little doubt that for PαMS as well as for PS in CH $(k_s)_\Theta$ is smaller than $[\eta]_\Theta$. This is likely to also hold true for other polymer–(Θ solvent) systems.

Temperature Dependence of the Friction Radius Expansion Factor in the Vicinity of the Θ Point. The sedimentation coefficient is factorized as follows:

$$s = m(1 - \bar{V}_p\rho_1)/\eta_1[f](1 + k_s c) \qquad (26)$$

Here m is the mass of the macromolecule.

For the temperature coefficient of s we write

$$\frac{\mathrm{d}\ln s}{\mathrm{d}T} = \frac{\mathrm{d}\ln s^0}{\mathrm{d}T} - \frac{c}{1 + k_s c}\left(\frac{\mathrm{d}k_s}{\mathrm{d}T} + k_s\frac{\mathrm{d}\ln\rho_1}{\mathrm{d}T}\right) \qquad (27a)$$

in which

$$\frac{\mathrm{d}\ln s^0}{\mathrm{d}T} = \frac{\mathrm{d}}{\mathrm{d}T}\ln\frac{1 - \bar{V}_p\rho_1}{\eta_1} - \frac{\mathrm{d}}{\mathrm{d}T}\ln[f] \qquad (27b)$$

The expansion coefficient of the solvent, $-\mathrm{d}\ln\rho_1/\mathrm{d}T$, allows for the thermal expansion of the solution.

The temperature coefficients for six molecular weights and for concentrations up to a concentration effect not larger than 0.25 have been plotted in Figure 4 in accordance with eq 27a. Owing to an appreciable residual heterogenity, the results for the largest M are less reliable than the other ones. The experiments show that the temperature coefficient may vary from near +2%/°C to −3%/°C within the usual concentration range for the sedimentation velocity analysis.

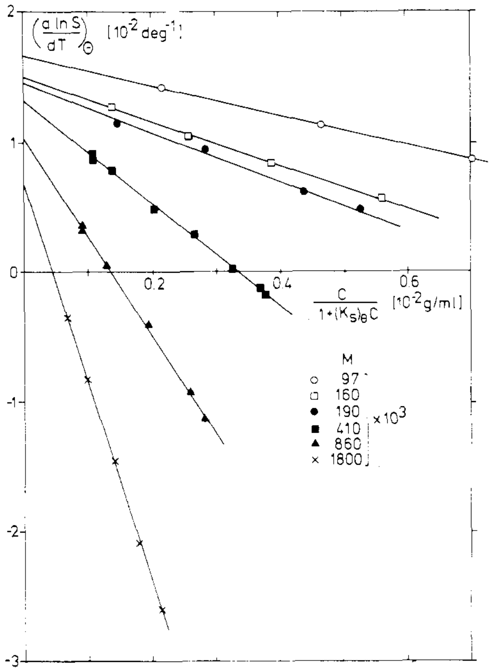

Figure 4. Temperature coefficient of the sedimentation coefficient for different molecular weights and concentrations. PS–CH, $T = \Theta$.

Table II
Intercepts and Slopes from Figure 4 and Standard Deviations[a]

$10^{-3}\times \bar{M}_w$	$10^2(\mathrm{d}\ln s^\circ/\mathrm{d}T)_\Theta$, deg^{-1}	SD	slope, mL g^{-1} deg^{-1}	SD	$(\mathrm{d}k_s/\mathrm{d}T)_\Theta$, mL g^{-1} deg^{-1}	$10^2(\mathrm{d}\ln k_s/\mathrm{d}T)_\Theta$, deg^{-1}
98	1.63	0.04	−1.09	0.07	1.11 ± 0.05	5.7 ± 0.4
160	1.49	0.02	−1.67	0.04	1.70 ± 0.04	6.9 ± 0.4
190	1.43_5	0.04	−1.83	0.1	1.86 ± 0.1	6.9 ± 0.5
411	1.30_5	0.02	−3.94	0.08	4.0 ± 0.1	10.0 ± 0.5
860	1.06	0.03	−7.8	0.02	7.9 ± 0.2	13.7 ± 0.7
1800	0.68	0.04	−15.4	0.3	15.5 ± 0.3	18.7 ± 1.0

[a] Temperature derivatives for k_s were derived from the slopes by using eq 27a. $\Theta = 34.5$ °C.

Least-squares straight lines have been fitted to the data points. The intercepts and slopes are given in Table II.

We first consider the intercepts.

We introduce the expansion factor α_f for the friction coefficient of the coiled polymer

$$[f] = [f]_\Theta\alpha_f \qquad (28)$$

Since $\alpha_f = 1$ ($T = \Theta$), it follows from (28) and (24) that

$$\left(\frac{\mathrm{d}\ln[f]}{\mathrm{d}T}\right)_\Theta = \frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}T}\ln\langle l_0^2\rangle + \left(\frac{\mathrm{d}\alpha_f}{\mathrm{d}T}\right)_\Theta \qquad (29)$$

In first-order perturbation theories for the real polymer chain, expansion factors are expanded in a power series of the interaction variable z. Since z is proportional to $M^{1/2}$ and vanishes for $T = \Theta$, we have

$$(\mathrm{d}\alpha_f/\mathrm{d}T)_\Theta = C_f M^{1/2} \qquad (30)$$

where C_f is independent of M.

Table III
Temperature Coefficients of α_η^3 and α_f for PS and PαMS in CH at $T = \Theta$ from Data of Different Sources

polym	$10^{-4}\overline{M}_w$	prepn[a]	Θ	$10^5(\mathrm{d}\alpha_\eta^3/\mathrm{d}T)_\Theta M^{-1/2}$, deg^{-1}	$10^5(\mathrm{d}\alpha_f/\mathrm{d}T)_\Theta M^{-1/2}$, deg^{-1}	ref
PS	360, 90	pf	35	3.6		28
	320	pf	35	3.3		29
	76.5	ap	34.6	3.1		30
	150	pf	34.5	3.0	(0.54 ± 0.05)	8
	11, 18, 42	ap	35	2.7		9
	10–86 (6 samples)	ap	34.5		0.87 ± 0.04	this work
PαMS	5–27 (4 samples)	ap	38.2	2.9		9

[a] pf = precipitation fractionation; ap = anionic polymerization.

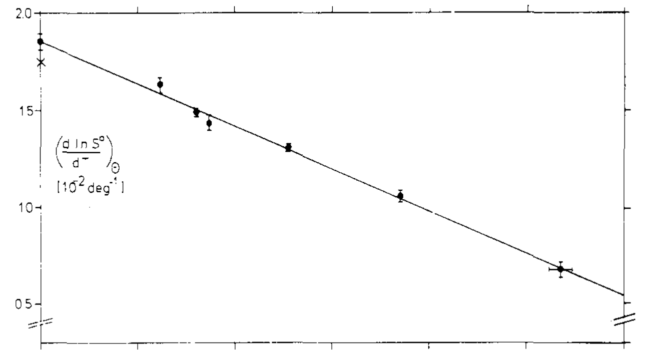

Figure 5. Temperature coefficients of sedimentation coefficients at infinite dilution vs. $\bar{M}_w^{1/2}$. PS–CH, $T = \Theta$.

In accordance with eq 27b, 29, and 30 we plotted $(\mathrm{d}\ln s^0/\mathrm{d}T)_\Theta$ vs. $M^{1/2}$, obtaining Figure 5. A weighted least-squares fitting of a linear equation yields

$$\left(\frac{\mathrm{d}\ln s^0}{\mathrm{d}T}\right)_\Theta = (1.85 \pm 0.03) \times 10^{-2} - (0.87 \mp 0.04) \times 10^{-5} M^{1/2}\ \mathrm{deg}^{-1} \quad (31)$$

As a test on the reliability of this result, the intercept was calculated by using the following independent data (all referring to 34.5 °C). The density measurements yielded a thermal expansion coefficient for CH $-(\mathrm{d}\rho_1/\mathrm{d}T)/\rho_1 = (1.24 \pm 0.01) \times 10^{-3}$ deg^{-1}. From the viscosity measurements the temperature coefficient for the kinematic viscosity was found to be $\{\mathrm{d}(\eta_1/\rho_1)/\mathrm{d}T\}/(\eta_1/\rho_1) = -(1.450 \pm 0.005) \times 10^{-2}$ deg^{-1}. The temperature coefficient for the partial specific volume of PS in CH was taken from Schulz and Hoffmann:[18] $(\mathrm{d}\bar{V}_p/\mathrm{d}T)/\bar{V}_p = (0.50 \pm 0.03) \times 10^{-3}$ deg^{-1}. From these values and from $\rho_1 = 0.7656$ g/mL and $\bar{V}_p = 0.934$ mL/g it is calculated that

$$\frac{\mathrm{d}}{\mathrm{d}T}\ln\frac{1-\bar{V}_p\rho_1}{\eta_1} = (1.76 \pm 0.01) \times 10^{-2}\ \mathrm{deg}^{-1} \quad (32)$$

For the temperature dependence of $\langle l_0^2\rangle$ we consulted a review (1969) by Flory.[25] Values of older dates have been abandoned and we now may rely on Orofino and Ciferri[26]

$$\tfrac{1}{2}\,\mathrm{d}\ln\langle l_0^2\rangle/\mathrm{d}T = (0.2 \pm 0.1) \times 10^{-3}\ \mathrm{deg}^{-1} \quad (33)$$

Taking the difference of (32) and (33), we have a value $(1.74 \pm 0.02) \pm 10^{-2}$ deg^{-1} on the ordinate in Figure 5. This is outside the error margin of (31). Although we think it is a reliable value, we excluded the crossed point from the least-squares fitting because of its different origin. We then have from the slope

$$(\mathrm{d}\alpha_f/\mathrm{d}T)_\Theta = (0.87 \pm 0.04) \times 10^{-5} M^{1/2}\ \mathrm{deg}^{-1} \quad (34)$$

Expansion Factors for Differently Defined Radii. The result for $(\mathrm{d}\alpha_f/\mathrm{d}T)_\Theta$ may be appreciated by comparing it with the temperature coefficient for the viscosity radius expansion factor α_η, making use of the respective first-order perturbation theories for the real chain polymer. Data ([η], T, M) are taken from the literature.

When the small temperature dependence of the unperturbed dimensions is neglected, $\alpha_\eta^3(T)$ may be equated to $[\eta]_T/[\eta]_\Theta$.

An equation of the Flory type

$$\alpha^5 - \alpha^3 = bz \quad (35)$$

is still a useful basis for plotting data ([η], T) that cover a large range in z.[27] For our purpose the value of b is irrelevant.

We plotted data ([η], T) for PS and PαMS in CH by several authors in the fashion $\alpha_\eta^5 - \alpha_\eta^3$ vs. $1/T$ and obtained the results listed in Table III.

Petrus et al.[8] as well as Kotera et al.[9] determined both [η] and s^0 in the vicinity of $T = \Theta$. We handled data for [f], derived from s^0, in the same manner as for [η]. No meaningful plot was obtained from Kotera's data. Only Petrus' data were compatible with the relation suggested by eq 35 (Table III, column 6).

From column 5 (Table III) and from our result (34), we obtain a value for the ratio of the coefficients C_1 and D_1 as defined by the expansions

$$\alpha_\eta^3 = 1 + C_1 z + \ldots \quad (36)$$

$$\alpha_f = 1 + D_1 z + \ldots \quad (37)$$

We find $C_1/D_1 = (3.0 \pm 0.2)/(0.87 \pm 0.04) = 3.4 \pm 0.3$.

The values $C_1 = 1.55$ and $D_1 = 0.416$ obtained by Kurata and Yamakawa[31] in their approximate first-order perturbation theory have often been cited. This theory is based on the Kirkwood–Riseman approach of polymer hydrodynamics.[22] It would follow from these values that $C_1/D_1 = 3.73$. Noda et al.[23] thought to have checked this value by determining the ratios $[\eta]_t/[\eta]_c$ and $[f]_t/[f]_c$ for PαMS in the good solvent toluene at 25 °C and the Θ solvent CH at 39 °C. From a log–log plot they concluded $C_1/D_1 = 2.4$.

Their procedure is incorrect, however, because for PαMS in toluene and for the range of M used, viz., $(4\text{–}122) \times 10^4$, z varies from 0.7 to 3.8 and exceeds the limits of validity of the linear relations 36 and 37. These limits are rated at $z \lesssim 0.15$ and $z \lesssim 0.4$, respectively (values for z have been calculated by using $z = 3.45 \times 10^{-2} M^{1/2}$, determined by Kato et al.[32]). To be sure, Stockmayer and Fixman[33] concluded that in the expansion of the third power of α, nonlinear terms in z are unimportant, but Berry[34] furnished proof to the contrary, using PS in toluene and decalin. In addition to this, 39 °C for PαMS in CH presumably is above Θ, as discussed earlier.

Recently (1977) Fujita et al.[35] calculated C_1 and D_1, using the same K–R formalism but avoiding the approximations adopted by Kurata and Yamakawa. From this work one would conclude that $C_1/D_1 = 1.295/0.591 = 2.19$.

The analysis by Fujita and co-workers was given a quick response by Shimada and Yamakawa,[36] who showed that

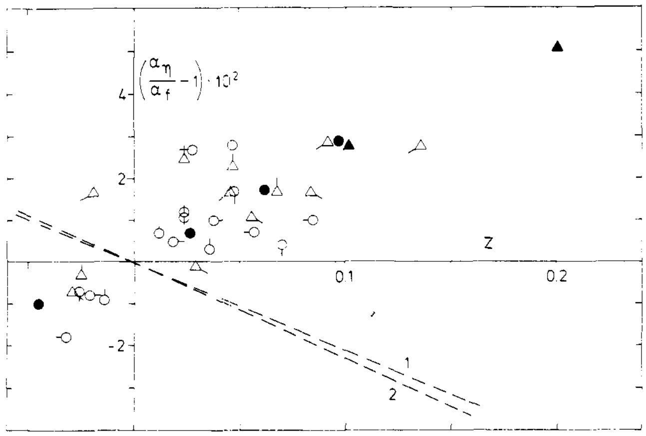

Figure 6. Ratio of the viscosity radius and friction radius expansion factors vs. z in the vicinity of $z = 0$. PS–CH:[8] (●) $M = 150 \times 10^4$. PS–CH:[9] (△) $M = 11 \times 10^4$; (△) $M = 17$; (△) $M = 42$. PαMS–CH:[9] (○) $M = 5 \times 10^4$; (○-) $M = 12$; (○) $M = 18$; (-○) $M = 27$. PS–TD:[47] (▲) $M = 39 \times 10^4$. Broken lines: tangents to curves at $z = 0$ predicted by theories: 1, Shimada and Yamakawa (both α_η and α_f); 2, Shimada and Yamakawa (α_η), Stockmayer and Albrecht (α_f).

the calculation of C_1 was incorrect. Applying numerical methods for solving the K–R-type integral integrations, they found $C_1 = 1.142$ and $D_1 = 0.593$, from which we have $C_1/D_1 = 1.93$.

The reliability of D_1 is in little doubt because the exact first-order perturbation theory value on the basis of the K–R formalism was established long before at 0.609 by Stockmayer and Albrecht.[37]

The comparatively small value for C_1 is supported by the work by Yamakawa and Tanaka,[38] who introduced a small excluded volume into the Zimm–Hearst theory[39,40] with no approximation. This resulted in $C_1 = 1.06$.

Thus, the first-order perturbation theories appear to settle down on a value for C_1/D_1 smaller than 2, which is in contrast to our experimental value 3.4.

Next, let us consider those few literature data about s^0 and $[\eta]$, which apply to the same monodisperse polymers in the same solvent, to temperatures near Θ, and which have been reported by the same authors.

Figure 6 shows a plot of α_η/α_f vs. z for PS of various molecular weights in CH and *trans*-decalin (TD) and for PαMS in CH. For the source material of s^0 and $[\eta]$ see the caption.

The ratios α_η/α_f have been evaluated by means of

$$\frac{\alpha_\eta}{\alpha_f} = \left(\frac{[\eta]}{[\eta]_\Theta}\right)^{1/3} \Big/ \frac{[f]}{[f]_\Theta} = \left(\frac{[\eta]}{[\eta]_\Theta}\right)^{1/3}\left(\frac{\eta_1 s^0}{1-\bar{V}_p\rho_1}\right)\Big/\left(\frac{\eta_1 s^0}{1-\bar{V}_p\rho_1}\right)_\Theta \quad (38)$$

The following additional data were used: $\eta_1(\mathrm{CH}) = 0.704_0 - 1.105 \times 10^{-2}(t-40) + 1.25 \times 10^{-4}(t-40)^2$ cP ($30 \lesssim t \lesssim 50$ °C); $\rho_1(\mathrm{CH}) = 0.759_6 - 1.21 \times 10^{-3}(t-40) - 2.4 \times 10^{-5}(t-40)^2$ g/mL; $\bar{V}_p(\mathrm{PS{-}CH}) = 0.932 + 5.0 \times 10^{-4}(t-30)$ mL/g;[18] $\bar{V}_p(\mathrm{P\alpha MS{-}CH}) = 0.883 + 5.0 \times 10^{-4}(t-30)$ mL/g. Values of η_1 and ρ_1 for TD and for $\bar{V}_p$(PαMS–TD) are given by Noda et al.[24]

From the values of $\bar{V}_p$ for the above three polymer–solvent systems, $\bar{V}_p$(PS–TD) was estimated at $0.937 + 5.0 \times 10^{-4}(t-30)$ mL/g. For $z(T, M)$ (PαMS–CH) we applied $z = 0.451 \times 10^{-2}(1-\Theta/T)M^{1/2}$, established by Kato and co-workers[32] from chain-expansion measurements (light scattering). For PS–CH and PαMS–CH not only the Θ points but also the values for $(\mathrm{d}\alpha_\eta^3/\mathrm{d}T)_\Theta$ are nearly equal (Table III). The same will hold for $(\mathrm{d}z/\mathrm{d}T)_\Theta$ which equals $C_1^{-1}(\mathrm{d}\alpha_\eta^3/\mathrm{d}T)_\Theta$ (eq 36). On this ground we felt it legitimate to use this expression for z also for PS–CH. Lacking a relation $z(T, M)$ for PS–TD determined by chain-expansion measurements, we used $z = 0.975 \times 10^{-2}(1-\Theta/T)M^{1/2}$, established by Berry[41] from the temperature dependence of A_2. It applies to PS in decalin of any cis–trans composition.

The data by Kotera and co-workers scatter but are in the first and third quadrants of the figure. No significance should be attached to the single point in the second quadrant because for one and the same sample α_η/α_f cannot be >1 both for $T > \Theta$ and $T < \Theta$.

The plot suggests that the initial slope of α_η/α_f with respect to z is 0.2 or 0.3, whereas the theoretical value by Shimada and Yamakawa is ${}^1/_3C_1 - D_1 = -0.212$. Taking $D_1 = 0.609$ by Stockmayer and Albrecht yields ${}^1/_3C_1 - D_1 = -0.228$.

We observe that combination of our result for $(\mathrm{d}\alpha_f/\mathrm{d}T)_\Theta$, eq 34, with Kato's expression for z(PαMS–CH) gives for D_1

$$(D_1)_{\mathrm{exptl}} = \left(\frac{\partial\alpha_f}{\partial T}\right)_\Theta \Big/ \left(\frac{\partial z}{\partial T}\right)_\Theta = 0.6 \quad (39)$$

in close agreement with the theory. Then, disagreement is found for C_1. Using $(\mathrm{d}\alpha_\eta^3/\mathrm{d}T)_\Theta = 3.0 \times 10^{-5}M^{1/2}$ deg^{-1}, we have $(C_1)_{\mathrm{exptl}} = 2.0$ in contrast to Shimada's $(C_1)_{\mathrm{theor}} = 1.14$.

We finally point out the real or seeming incongruity in the sequence of linear coefficients D_1, ${}^1/_3C_1$, ... in the series expansions for the expansion factors for the differently defined radii for a chain polymer.

Let us compare these coefficients with the ratio of the radii in the Θ condition.

The volume of the viscosity-equivalent impermeable sphere follows from the definition of the intrinsic viscosity and Einstein's equation for the viscosity of a dilute suspension of spheres and is

$$V_\eta = 2[\eta]M/5N_A \qquad ([\eta] \text{ in mL/g}) \quad (40)$$

Its radius is

$$R_\eta = (3[\eta]M/10\pi N_A)^{1/3} \quad (41)$$

Using Stokes' equation for the radius of the friction-equivalent sphere

$$R_f = [f]/6\pi \quad (42)$$

we get

$$\frac{R_\eta}{R_f} = 6\pi\left(\frac{3}{10\pi N_A}\right)^{1/3}\frac{([\eta]M)^{1/3}}{[f]} \quad (43)$$

Substituting for N_A and well-known expressions for $[f]$, eq 24 and 28, and $[\eta]$

$$[\eta] = \Phi_0(\langle l_0^2\rangle/M)^{3/2}\alpha_\eta^3 \quad (44)$$

we obtain

$$R_\eta/R_f = 1.020 \times 10^{-7}\beta \quad (45)$$

in which $\beta = \beta_0(\alpha_\eta/\alpha_f)$ with $\beta_0 = \Phi_0^{1/3}P^{-1}$. β is the Scheraga–Mandelkern constant,[42] which is not truly a constant, unless $\alpha_\eta = \alpha_f$ for any z.

The theoretical values for Φ_0 scatter[43] but are in such a range that $10^{-7}\beta_0$ and $(R_\eta/R_f)_\Theta$ are well over unity.

For a check using experimental data, we eliminate $[f]$ in favor of the sedimentation coefficient. Substituting from (26) ($c \rightarrow 0$) we have

$$\beta = N_A[\eta]^{1/3}\eta_1 s^0/(1 - \bar{V}_p\rho_1)M^{2/3} \qquad (46)$$

For PS in CH we use the well-established relations $[\eta]_\Theta = 0.084M^{1/2}$ mL/g[17,44] and $s_\Theta{}^0 = 1.51 \times 10^{-5}M^{1/2}$ s (vide infra), along with values for η_1, ρ_1, and $\bar{V}_p$ stated previously. Thus $(R_\eta/R_f)_\Theta$ becomes 1.095. Values in the range 1.10–1.13 result for PαMS–CH by using the relations $[\eta]_\Theta(M)$ and $s_\Theta{}^0(M)$ determined by Cowie et al.,[45,46] those by Abe et al.,[12] or those by Noda et al.[24,48] For PαMS–TD a value 1.17 is found.[24,48]

For a random-flight chain the radius of gyration R_g equals $(\langle l_0{}^2\rangle/6)^{1/2}$, while according to eq 24 and 42, $R_f = 0.271(\langle l_0{}^2\rangle)^{1/2}$. We thus have

$$R_f{:}R_\eta{:}R_g{:}\tfrac{1}{2}(\langle l_0{}^2\rangle)^{1/2} = 1{:}1.1{:}1.50{:}1.84 \qquad (T = \Theta) \qquad (47)$$

The exact or claimed nearly exact first-order perturbation theory values for the linear coefficients in the series expansions of the respective expansion factors are

$$D_1{:}\tfrac{1}{3}C_1{:}B_1{:}A_1 = 0.609{:}\frac{1.142}{3}{:}\frac{67}{105}{:}\frac{2}{3} \approx 0.61{:}0.38{:}0.64{:}0.67 \qquad (48)$$

An incongruity with respect to the value of C_1 is suggested from a comparison of (48) with (47).

If the expansion of a chain polymer were uniform, the ratio of the various radii would be independent of z, and the coefficients D_1, $^1/_3C_1$, ... would be equal with a value near 0.64, in spite of the fact that D_1 and C_1 are also determined by hydrodynamic factors, whereas B_1 and A_1 are not. The expansion is not uniform, however. The expansion factor for the root-mean-square distance between segments of equal number from the chain ends increases with the enclosed contour length.[49] Consequently, the coefficients have different values. A difference so large, however, as is realized with a value 0.38 for $^1/_3C_1$, combined with the experimental findings shown in Figure 6, raises doubts about the reliability of the current theories for α_η.

More experimental evidence should be obtained about $(\mathrm{d}\alpha_\eta{}^3/\mathrm{d}T)_\Theta$ and $(\mathrm{d}\alpha_f/\mathrm{d}T)_\Theta$ for various polymer–solvent systems. Since no proof has been given that an equation like (35) holds true for α_f, more reliable results for $(\mathrm{d}\alpha_f/\mathrm{d}T)_\Theta$ will be obtained by using the differential sedimentation method than by establishing individual values for $[f]$ in the vicinity of $T = \Theta$.

Temperature Dependence of k_s near the Θ Point. We next consider the slopes of the lines in Figure 4. In the expression for the slope, eq 27a, the magnitude of the term representing the thermal expansion of the solutions is very small. Besides, the two terms present are of different order in M. For these reasons the numerical values for the slopes were corrected for the thermal expansion, using $(k_s)_\Theta$ from eq 21 and d ln $\rho_1/\mathrm{d}T$ stated earlier, to yield $(\mathrm{d}k_s/\mathrm{d}T)_\Theta$ (Table II). It is seen from a plot of this derivative that it increases almost proportionally with M (Figure 7). The straight line fitted to the data points is given by

$$(\mathrm{d}k_s/\mathrm{d}T)_\Theta = (0.3 \pm 0.1) + (0.87 \mp 0.02) \times 10^{-5}M \text{ mL g}^{-1} \text{ deg}^{-1} \qquad (49)$$

The validity of (49) for small M is doubtful because $\mathrm{d}k_s/\mathrm{d}T$ should vanish together with M. It should be noted that the apparent intercept is much larger than the small intercept resulting from the asymptotic character of the linear relationship which holds for large chains.

It follows from eq 34 and from the values for $(k_s)_\Theta$ and $(\mathrm{d}k_s/\mathrm{d}T)_\Theta$ in Tables I and II that the rate of change of ln k_s with the temperature is much larger than that of α_f. This is due to the fact that α_f represents a linear expansion whereas k_s increases not only through the cubic expansion of individual chain molecules but also by their mutual repulsion. In addition to this, the latter contribution is much larger.

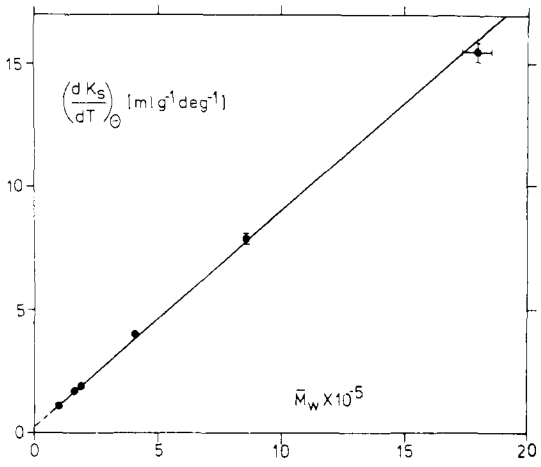

Figure 7. Temperature dependence of the coefficient for concentration dependence of the sedimentation coefficient vs. $\bar{M}_w$. PS–CH, $T = \Theta$.

A further analysis of $(k_s)_\Theta$ and $(\mathrm{d}k_s/\mathrm{d}T)_\Theta$ will be based on equations to be developed in a subsequent paper.[19]

Although thus far two details of Figures 5 and 7 are unexplained, we may conclude that the good performance of the differential method has been demonstrated. The reliable experimental data about the concentration dependence of the sedimentation coefficient will enable us to test theories of this matter more precisely.

The high rate of change of the concentration dependence of s with the temperature is a sensitive measure of the temperature dependence of the excluded volume of the polymer coils. However, it is a disadvantage for establishing a quantitative relationship that it involves both intermolecular and intramolecular interactions. This complication distinguishes it from temperature effects observed in osmometry and light scattering, where systems are in thermodynamic equilibrium and the temperature dependence of the second virial coefficient at the Θ point is only determined by the intermolecular interaction.

Acknowledgment. I thank Professor Dr. A. J. Staverman for his critical reading of manuscripts and valuable suggestions.

Appendix (Equation 9)

In the absence of a pressure effect the concentration at the theoretical boundary point is given by the well-known square dilution rule

$$\Theta_i = (r_0/r_i)^2 = (1 + \xi_i)^{-1} \qquad (i = 1, 2) \qquad (1')$$

Since $\xi_i = \xi_i(\tau, \gamma_i)$, Θ_i depends implicitly on γ_i through ξ_i.

It has been shown[2,50] that in the event of a pressure effect without a concentration effect

$$\Theta_i = (1 + m\xi_i)/(1 + \xi_i) \qquad (i = 1, 2) \qquad (2')$$

We examine the explicit dependence of Θ_i on γ_i in addition to (2′) when the pressure and concentration effects go together.

Since the added part vanishes whenever γ_i or m or ξ_i is zero, it will be of the order $\gamma_i m\xi_i{}^n$, where n is a positive integer. We now go in search of its value.

Let ξ be the reduced cell coordinate and ξ^* the position of the boundary point. The latter follows from integration of eq 6. Then the relationship between the running and

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the local derivative of the concentration at the boundary point is

$$\frac{d\Theta^*}{d\xi^*} = \left[\frac{\partial\Theta}{\partial\xi} + \frac{\partial\Theta}{\partial\tau}\frac{d\tau}{d\xi}\right]^* \qquad (3')$$

In the right-hand member the asterisk indicates that the derivatives must be specified for the boundary point.

In view of the initial conditions $\Theta = 1$ ($\tau = 0$, $\xi > 0$) and $\xi^* = 0$ ($\tau = 0$), we have

$$\partial\Theta/\partial\xi = 0 \qquad (\xi^* = 0) \qquad (4')$$

The balance equation for the solute, going with eq 6, is

$$\frac{\partial\Theta}{\partial\tau} = -\frac{\partial}{\partial\xi}\left\{\frac{(1+\xi)\Theta}{(1+m\xi)(1+\gamma\Theta)}\right\} \qquad (5')$$

Expanding the right-hand member and using (4′), we observe that

$$(\partial\Theta/\partial\tau)^* = -(1-m)/(1+\gamma) \qquad (\xi^* = 0) \qquad (6')$$

It follows from (6) that

$$d\xi^*/dT = (1+\gamma)^{-1} \qquad (\xi^* = 0) \qquad (7')$$

Substituting (4′), (6′), and (7′) into (3′) we obtain

$$d\Theta^*/d\xi^* = -(1-m) \qquad (\xi^* = 0) \qquad (8')$$

This initial value holds good irrespective of the presence of a concentration effect. It is fulfilled by (2′). If (2′) were to be augmented by a term of the order $\gamma_i m\xi_i$, then condition 8′ could not be satisfied. On this ground we conclude that $n \geq 2$.

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Sedimentation Equilibrium of Highly Nonideal Solutions of Polydisperse Polymers

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ABSTRACT: A new method of analysis is proposed for determination of the average molecular weight of a polymer sample, of its polydispersity, and of the thermodynamic characteristics of its solution. The method involves only a single sedimentation equilibrium experiment in the ultracentrifuge and is applicable even to highly nonideal solutions. It is based on the assumptions that (1) the distribution function of the polymer sample is reasonably well described by the unimodal function of the Schulz–Zimm type and that (2) the thermodynamic behavior of the solution obeys the same formula which was found useful for monodisperse samples. The method yielded plausible results both for highly nonideal solutions of polystyrene samples with a narrow distribution of molecular weights and for unfractionated samples of polyacrylamide with a broader distribution.

Among the methods used for studying polymer solutions, the method of sedimentation equilibrium is potentially the most precise. Using interference optics, sapphire cell windows, and an automated plate reader, we can, under favorable circumstances, measure the profile (one hundred and more experimental points) of concentration and concentration gradient within the cell with a precision of 1–2%. Why is then this method so rarely used for the

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