

Concentration Dependence of the Sedimentation Coefficient of Flexible Macromolecules in Dilute Solution: Poly(α -methylstyrene) and Polystyrene^{*,**}

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ABSTRACT: The coefficient k_s in the expression for the sedimentation coefficient, $1/S = (1/S_0)(1 + k_s c + \dots)$, where S and S_0 are the sedimentation coefficients at finite polymer concentration c and at infinite dilution, respectively, was investigated experimentally for the systems of poly(α -methylstyrene) and polystyrene in cyclohexane in the vicinity of the θ -condition.

The k_s -values at the θ -condition were positive and were expressed by a linear function of the square root of molecular weight. The behavior of k_s in the region away from the θ -condition could be satisfactorily described according to the theory of Pyun and Fixman when certain results obtained regarding the relationship between the segment—segment interaction parameter and the expansion factor were used.

KEY WORDS Concentration Dependence / Dilute Solution / Expansion Factor / Frictional Properties / Poly(α -methylstyrene) / Polystyrene / Sedimentation / θ -Temperature /

The concentration dependence of the sedimentation coefficient is expressed by the following form

$$1/S^0 = (1/S_0^0)(1 + k_s c + \dots) \quad (1)$$

where S^0 and S_0^0 are the sedimentation coefficient at a finite polymer concentration c , and at infinite dilution, respectively; k_s may be considered to be a parameter of the hydrodynamic interaction between sedimenting polymer molecules.

Some theoretical treatments, each employing a different model, have been reported for k_s .^{1,2} These theories, however, did not coincide well with experimental results, which indicated that

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k_s in a poor or θ -solvent was smaller than that in a good solvent and that k_s decreased with decreasing temperature.

In 1962, Yamakawa proposed a theory³ concerning k_s on the basis of the Kirkwood—Riseman approach and stated that k_s vanished at the θ -condition and increased with increasing temperature. On the other hand, Pyun and Fixman⁴ treated the macromolecular solutes as suspended spheres, taking account of the long-ranged hydrodynamic interaction, and stated that k_s increased with increasing temperature, having a positive value at the θ -condition.

There has been a limited amount of experimental data which permitted the determination of the temperature dependence of k_s .⁵ The authors therefore investigated the temperature dependence of k_s in the vicinity of θ -condition, and attempted to describe the data as a function of the expansion factor. A detailed comparison of the experimental results with the theory of Pyun and Fixman was also made. For this purpose, sedimentation and viscosity of poly(α -methylstyrene) and polystyrene in cyclohexane were measured at several temperatures above and

below the θ -point.

EXPERIMENTAL

Samples

The four poly(α -methylstyrene) samples used were anionically polymerized at Nagoya University and were kindly supplied by Prof. M. Nagasawa. The polystyrene samples used, which, as shown below, had very narrow molecular weight distributions, were commercially distributed by Pressure Chemicals as the standard samples for gel-permeation chromatography.

Solvents

Cyclohexane was purified by the usual method and fractionally distilled over sodium. The fraction obtained in the range of bp from 80.7 to 80.8°C was used [n_D^{25} 1.4233, d^{25} 0.7743(g/ml)].

Purified toluene was obtained by the usual method [bp 110.5–110.6°C, n_D^{25} 1.4942, d^{25} 0.8629(g/ml)]. θ -Temperature: Determination of the θ -temperature for the poly(α -methylstyrene)—cyclohexane system was carried out by using a Shimadzu Light-Scattering Photometer with a poly(α -methylstyrene) sample. This sample was prepared with BF_3 catalyst at Kyoto University and kindly supplied by Prof. S. Okamura. A value of $38.2 \pm 0.6^\circ\text{C}$ was obtained for the θ -temperature of poly(α -methylstyrene) in cyclohexane from measurements at temperatures within the range 34 to 45°C. This value is very close to the 38.0°C reported previously from this laboratory⁶ and falls within the ranges reported by several other investigators.⁷⁻⁹

The θ -temperature for the polystyrene—cyclohexane system was assumed to be 35.0°C, as determined from the light-scattering measurement.⁶

Molecular-Weight Determination

Number-Average Molecular-Weight. Number-average molecular weights were determined in toluene by using two kinds of apparatus. One was a Mechrolab High Speed Membrane Osmometer, model 502, which was used for poly(α -methylstyrene) samples at $37.0 \pm 0.2^\circ\text{C}$, and the other a Hallikainen Automatic Osmometer, model 1361 BS 1, for polystyrene samples at $35.0 \pm 0.2^\circ\text{C}$.

Weight-Average Molecular Weight. Weight-average molecular weights were determined by using an Aminco Light-Scattering Photometer,

at $38.0 \pm 0.2^\circ\text{C}$ for poly(α -methylstyrene)—cyclohexane and at $35.0 \pm 0.2^\circ\text{C}$ for polystyrene—cyclohexane. The refractive index increment, dn/dc , for 436 $m\mu$ unpolarized light was 0.204 ml/g for poly(α -methylstyrene) in cyclohexane at 38.0°C and 0.181 ml/g for polystyrene in cyclohexane at 35.0°C.¹⁰

Partial Specific Volume. The partial specific volume of poly(α -methylstyrene) in cyclohexane at 38.0°C was found to be 0.889 ml/g with a pycnometer having a volume of *ca.* 12 ml, which is very close to a reported value of 0.886 ml/g at 39.0°C.⁷

A value of 0.928 ml/g was used for polystyrene in cyclohexane at 35.0°C which had been reported by Mandelkern, *et al.*¹⁰

Sedimentation Measurement. Sedimentation velocity experiments were carried out in cyclohexane at five temperatures above and below the θ -point, using a Hitachi Model UCA-1 ultracentrifuge equipped with a schlieren optical system. Temperatures were controlled within $\pm 0.2^\circ\text{C}$ and a 12 mm-centerpiece used. In all runs, the distance traversed by a schlieren peak was kept shorter than 3 mm to reduce the corrections for the pressure and radial dilution effects.

For organic solvents the pressure effect upon sedimentation rate is generally appreciable due to their large compressibilities. It is usually corrected by using the following (Fujita's) equation:¹¹

$$S^{\text{app}} = S^0 \{1 - G[(r_p/r_m)^2 - 1]\} \quad (2)$$

where

$$S^{\text{app}} = \ln(r_p/r_m) / \{\omega^2(t - t_0)\} \quad (3)$$

Here S^{app} is the sedimentation coefficient at a time t , S^0 the sedimentation coefficient for the initial concentration at 1 atm., r_p the position of the maximum refractive index gradient, r_m the position of the meniscus, ω the angular velocity, t_0 the initial time correction, and G the parameter which includes the pressure and radial dilution effects.

If S^{app} is plotted against $(r_p/r_m)^2 - 1$ according to eq 2, the corrected sedimentation coefficient S^0 can be determined from the intercept. However, since the initial time correction t_0 is not known in advance, it is quite difficult to determine S^0 without ambiguity. In this work, t_0

was determined by extrapolating the position of the maximum index gradient to that of the meniscus, since a linear relationship was found experimentally to exist between $\ln(r_p/r_m)$ and time t as long as the sedimentation distance remained small.

A new method, called the "best fit" method, was proposed recently to determine a reasonable value of S^0 .^{7,12} In this method, S^{app} is assumed to be a function of t_0 as shown in eq 3, since quantities such as r_p , r_m , ω , and t are directly obtained. Then, both S^0 and t_0 which give best fit to eq 2 are determined from the plots of S^{app} vs. $(r_p/r_m)^2 - 1$ so that the standard deviation of the difference between the left-hand term and right-hand term of eq 2 becomes a minimum.

For comparison of the empirical method used with the best fit method,^{7,12} the authors applied the latter method to the data obtained at 44100 rpm and at 37600 rpm for poly(α -methylstyrene) sample of PMS-227 in cyclohexane (38.2°C, $c_0 = 0.304$ g/dl). The relative differences in the values of S^0 from the two methods were less than 3% at 44100 rpm and 2% at 37600 rpm. It therefore appeared that the data obtained by the present method were reasonable.

When ultracentrifugations are carried out at different speeds, it is necessary to know how much the S^0 -value is affected by rotor speed.

Figure 1 shows the results for poly(α -methylstyrene) sample PMS-227 in cyclohexane (38.2°C, $c_0 = 0.304$ g/dl) at different velocities. It is found from Figure 1 that the intercepts of the straight lines for different velocities do not agree perfectly with each other, but the relative differences in S^0 -values are less than 3%. Therefore, it seems that the sedimentation coefficient at initial con-

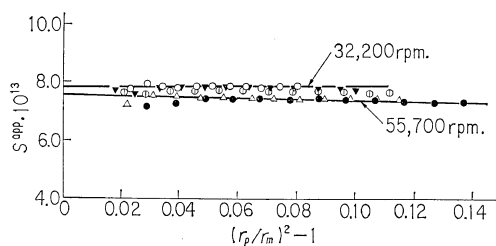


Figure 1. Plots of S^{app} vs. $(r_p/r_m)^2 - 1$ for PMS-227 in cyclohexane (38.0°C, $c_0 = 0.304$ g/dl) at different speeds: \circ , 32200 rpm; \blacktriangledown , 37600 rpm; \odot , 44100 rpm; \triangle , 51900 rpm; \bullet , 55600 rpm.

Table I. Experimental conditions in sedimentation measurements

Sample	Rotor speed, rpm	Temp, °C
Poly(α -methylstyrene)		
PMS-6	about 55430	34.0, 38.2, 42.0, 46.0, 50.0
PMS-03	about 47300	"
PMS-227	about 43700	"
PMS-10	about 37290	"
Polystyrene		
PS-9	about 51200	30.0, 35.0, 40.0, 45.0, 50.0
PS-16	about 43700	"
PS-41	about 37290	33.0, 35.0, 40.0, 45.0, 50.0

centration is not greatly affected by the velocity employed. In this study, the authors selected the optimum velocities by taking into account the molecular weight as shown in Table I.

The sedimentation coefficient at infinite dilution, S_0^0 , and the concentration dependence coefficient, k_s , were determined by using corrected values of S^0 obtained at several concentrations through extrapolation to infinite dilution according to eq 1.

Viscosity Measurement. Measurements of intrinsic viscosity were carried out at the same temperatures as in the sedimentation measurements by using an Ubbelohde dilution type viscometer. The intrinsic viscosity, $[\eta]$, and Huggins' constant, k' , were determined by use of the Huggins' equation.

RESULTS

Molecular-Weight Heterogeneity. The values of number-average molecular weight (\bar{M}_n) and weight-average molecular weight (\bar{M}_w) for each sample are summarized in Table II together with the second virial coefficient B_2 from osmotic pressure and A_2 from light scattering. The \bar{M}_w/\bar{M}_n -values given in the last column of Table II are very close to unity. It is therefore assumed that all samples used in this work were sufficiently homogeneous with respect to molecular weight.

Sedimentation Coefficient. The results summarized in Tables III and IV show that the S_0^0 -values for these samples increase with increasing temperature. This tendency is reasonable because

Table II. Characterization of samples

Sample	Osmotic-pressure measurement ^a		Light-scattering measurement ^b		\bar{M}_w/\bar{M}_n
	$\bar{M}_n \times 10^{-4}$	$B_2 \times 10^4$	$\bar{M}_w \times 10^{-4}$	$A_2 \times 10^4$	
Poly(α -methylstyrene)					
PMS-6	—	—	4.9	-0.5	—
PMS-03	11.9	4.0	12.1 ^c	0.0 ^c	1.0 ₃
PMS-227	—	—	18.3 ^c	0.0 ^c	—
PMS-10	25.9	3.5	26.8 ^c	0.0 ^c	1.0 ₃
Polystyrene					
PS-9	10.6	6.9	10.9	0.0	1.0 ₃
PS-16	15.9	4.3	17.0	0.0	1.0 ₆
PS-41	37.6	4.3	42.2	0.0	1.1 ₂

^a In toluene at 37.0°C for poly(α -methylstyrene) and at 35.0°C for polystyrene.

^b In cyclohexane at 38.0°C for poly(α -methylstyrene) and at 35.0°C for polystyrene.

^c Determined in cyclohexane at 38.0°C by A. Wada in this laboratory.

the sedimentation coefficient should increase with increasing temperature owing to the reduction in solvent viscosity as well as in density.

(1) In Figure 2, the values of $\log S_{0\theta}^0$ for poly(α -methylstyrene) are plotted against $\log \bar{M}_w$, together with the values obtained by Nagasawa, *et al.*,⁷ and by Kurata, *et al.*⁸ Although the values by these two groups were obtained in cyclohexane at 39.0°C, it is fair to say that the present data agree reasonably well with them.

The relationship between $S_{0\theta}^0$ and \bar{M}_w was approximated by the following form*

$$S_{0\theta}^0 = 1.93 \times 10^{-15} \bar{M}_w^{\frac{1}{2}} \quad (4)$$

(2) The results of $S_{0\theta}^0$ for the polystyrene—cyclohexane system at 35.0°C are plotted against \bar{M}_w in Figure 3, wherein the reported data^{5,10,13-15} for more heterogeneous samples are also included for comparison.

It is found from Figure 3 that the present data are in close agreement with those of other studies. The authors determined the following relationship between $S_{0\theta}^0$ and \bar{M}_w by fitting a straight line to these and previous data

* The relationships for poly(α -methylstyrene) in cyclohexane at 39°C were reported to be $S_{0\theta}^0 = 2.04 \times 10^{-15} \bar{M}_w^{\frac{1}{2}}$ by Nagasawa, *et al.*,⁷ and $S_{0\theta}^0 = 2.00 \times 10^{-15} \bar{M}_w^{\frac{1}{2}}$ by Kurata, *et al.*,⁸ respectively.

Table III. Results of sedimentation and viscosity measurements for Poly(α -methylstyrene) in cyclohexane near the θ -temperature

Sample	$T, ^\circ\text{C}$	$S_{0\theta}^0(\text{sved})$	$k_s, \text{dl/g}$	$[\eta], \text{dl/g}$	k'
PMS-6	34.0	3.9 ₀	0.1 ₄	0.16 ₁	1.0
	38.2(θ) ^c	4.2 ₃	0.1 ₇	0.16 ₆	0.8 ₆
	42.0	4.5 ₀	0.2 ₀	(0.17 ₀) ^a	—
	46.0	4.8 ₂	0.2 ₀	0.17 ₃	0.7 ₁
	50.0	5.0 ₉	0.2 ₁	0.17 ₇	0.6 ₀
PMS-03	34.0	6.0 ₉	0.2 ₃	(0.24 ₄) ^b	—
	38.2(θ) ^c	6.5 ₆	0.2 ₇	0.25 ₃	0.7 ₄
	42.0	6.9 ₉	0.3 ₄	0.26 ₀	0.7 ₉
	46.0	7.4 ₇	0.3 ₈	0.26 ₈	0.6 ₈
	50.0	8.0 ₃	0.4 ₁	0.28 ₀	0.5 ₆
PMS-227	34.0	7.8 ₈	0.2 ₄	0.31 ₆	0.9 ₂
	38.2(θ) ^c	8.4 ₇	0.3 ₃	0.33 ₀	0.7 ₇
	42.0	9.0 ₁	0.3 ₇	0.34 ₃	0.7 ₇
	46.0	9.6 ₃	0.4 ₂	0.35 ₆	0.7 ₁
	50.0	10.0	0.4 ₄	0.37 ₆	0.6 ₁
PMS-10	34.0	9.2 ₉	0.3 ₂	0.36 ₁	0.9 ₁
	38.2(θ) ^c	10.1	0.4 ₆	0.38 ₂	0.8 ₁
	42.0	10.8	0.5 ₃	0.39 ₄	0.7 ₉
	46.0	11.3	0.5 ₆	0.41 ₄	0.6 ₈
	50.0	12.0	0.5 ₇	0.43 ₀	0.7 ₀

^a Interpolated value.

^b Extrapolated value.

^c (θ), θ -temperature.

Table IV. Results of sedimentation and viscosity measurements for polystyrene in cyclohexane near the θ -temperature

Sample	$T, ^\circ\text{C}$	$S_{0\theta}^0(\text{sved})$	$k_s, \text{dl/g}$	$[\eta], \text{dl/g}$	k'
PS-9	30.0	4.5 ₀	0.1 ₉	0.24 ₄	0.6 ₇
	35.0(θ)	4.8 ₈	0.2 ₆	0.25 ₄	0.6 ₈
	40.0	5.4 ₄	0.3 ₆	0.26 ₄	0.7 ₃
	45.0	5.8 ₉	0.4 ₁	0.27 ₃	0.7 ₀
	50.0	6.2 ₈	0.4 ₄	0.28 ₆	0.5 ₉
PS-16	30.0	5.9 ₇	0.2 ₁	0.30 ₈	0.5 ₈
	35.0(θ)	6.4 ₈	0.3 ₃	0.33 ₈	0.5 ₀
	40.0	6.9 ₂	0.3 ₆	(0.35 ₅) ^a	—
	45.0	7.5 ₈	0.4 ₆	(0.37 ₀) ^a	—
	50.0	8.2 ₄	0.5 ₅	0.38 ₀	0.4 ₆
PS-41	33.0	10.0	0.4 ₄	(0.49 ₆) ^b	—
	35.0(θ)	9.9 ₁	0.3 ₇	0.51 ₃	0.7 ₁
	40.0	10.9	0.6 ₄	0.56 ₄	0.6 ₁
	45.0	11.9	0.8 ₃	0.59 ₅	0.5 ₈
	50.0	12.7	0.9 ₈	0.63 ₀	0.6 ₆

^a Interpolated value.

^b Extrapolated value.

^c (θ), θ -temperature.

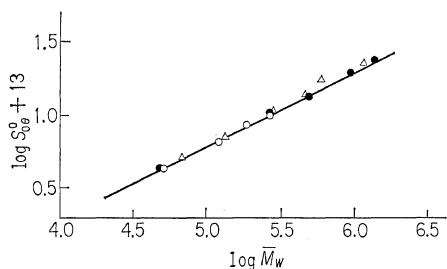


Figure 2. Double logarithmic plots of S_{θ}^0 vs. \bar{M}_w for poly(α -methylstyrene) in cyclohexane at the θ -condition: \circ , this work (38.2°C); \triangle , Nagasawa, *et al.*⁷; \bullet , Kurata, *et al.*⁸; solid line, obtained from the data in this work.

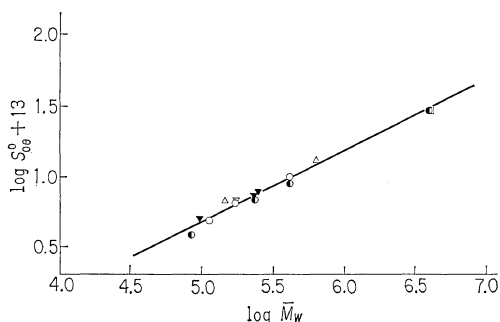


Figure 3. Double logarithmic plots of S_{θ}^0 vs. \bar{M}_w for polystyrene in cyclohexane at the θ -temperature (35.0°C): \circ , this work; \triangle , Wales, *et al.*¹⁴; \square , McIntyre, *et al.*¹⁰; \blacktriangledown , Billick¹⁵; \bullet , Homma, *et al.*¹³; ∇ , Billick⁵; solid line, obtained from the data both in this work and in earlier reports.

$$S_{\theta}^0 = 1.52 \times 10^{-15} \bar{M}_w^{\frac{1}{2}} \quad (5)$$

Intrinsic Viscosity. The results from the viscosity measurements are listed in Tables III and IV for poly(α -methylstyrene) and polystyrene, respectively.

(1) The $[\eta]_{\theta}$ -values for poly(α -methylstyrene) obtained in this work are plotted against \bar{M}_w in Figure 4 which also includes the data obtained at 39°C by Nagasawa, *et al.*⁷ and at 37.0°C by Cowie, *et al.*⁹ Figure 4 shows that all the plotted data agree with each other in spite of the temperature difference.

(2) In Figure 5, the values of $[\eta]_{\theta}$ for polystyrene are plotted against \bar{M}_w plus those obtained by other investigators^{10,13} in cyclohexane at 35.0°C. It can be seen that the data from this work agree with those of earlier authors.

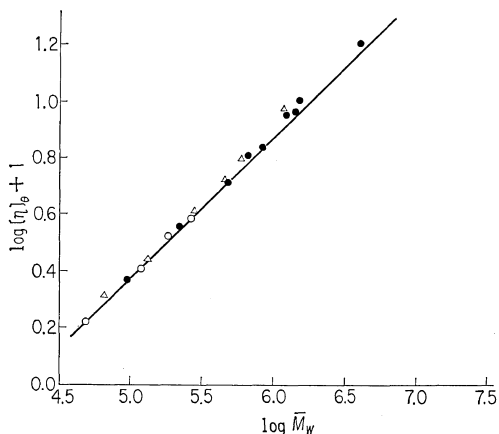


Figure 4. Double logarithmic plots of $[\eta]_{\theta}$ vs. \bar{M}_w for poly(α -methylstyrene) in cyclohexane at the θ -condition: \circ , this work (38.2°C); \triangle , Nagasawa, *et al.*⁷ (39.0°C); \bullet , Cowie, *et al.*⁹ (37.2°C); solid line, obtained from the data in this work.

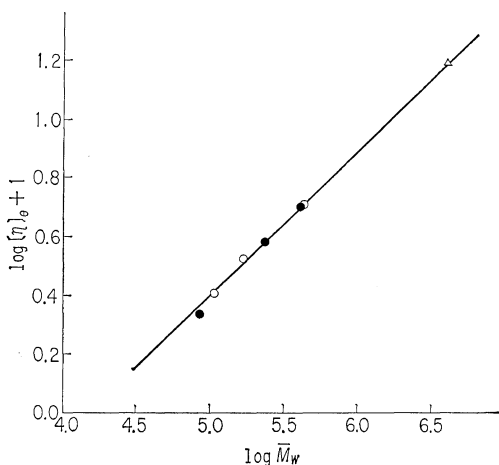


Figure 5. Double logarithmic plots of $[\eta]_{\theta}$ vs. \bar{M}_w for polystyrene in cyclohexane at the θ -temperature (35.0°C): \circ , this work; \triangle , McIntyre, *et al.*¹⁰; \bullet , Homma, *et al.*¹³; solid line, obtained from the data in this work.

Variation of k_s -Value with Temperature. The results listed in Tables III and IV show that k_s for each sample is apparently positive at the θ -point and tends to increase with increasing temperature.

DISCUSSION

In the introductory section, it was pointed out

that two different theories were recently proposed for the description of k_s -behavior in dilute polymer solution, one by Yamakawa³ and the other by Pyun and Fixman.⁴

According to Yamakawa,³ k_s is given by

$$k_s = 1.65[\eta]\lambda(x_1) \log(1 + 5.73x_1) \quad (6)$$

where

$$x_1 = z/\alpha_\eta^3.$$

Here $\lambda(x_1)$ is a function of x_1 , z is the parameter of volume exclusion, and α_η is the viscosity expansion factor. This equation shows that k_s vanishes at the θ -condition ($x_1=0$), and that it increases with increasing temperature, because $\lambda(x_1)$ is nearly constant for x_1 near the θ -condition.

According to Pyun and Fixman,⁴ k_s in the vicinity of θ -condition can be simply expressed by the following form, if higher terms in the series expansion of their original equation are neglected

$$k_s = C_1(a^3/M)(K_0 + K_1x_2) \quad (7)$$

where

$$x_2 = C_2(1 - \theta/T)a^{-3}.$$

Here C_1 , C_2 , K_0 , and K_1 are positive constants, and a is the radius of a polymer chain. According to this theory, k_s increases with increasing temperature and has a positive finite value at the θ -condition.

Therefore, we find that the essential difference between the above-mentioned two theories is in the description of the k_s -behavior at the θ -condition. From the present experimental results in the vicinity of θ -conditions for both poly(α -methylstyrene) and polystyrene, it is found that the k_s -values at the θ -condition are positive (see Tables III and IV). This result as well as those recently obtained by the other investigators^{5,7,8,12} supports the theory of Pyun and Fixman rather than the Yamakawa theory.

Treatment by the Pyun and Fixman Theory

According to Pyun and Fixman,⁴ the detailed expression for k_s reads

$$k_s = (4/300)(M/N\pi)^2[(1 - \bar{v}\rho_0)/(6\eta_0 S_0^0)]^3[7.16 - \kappa(A)] \quad (8)$$

where M is the polymer molecular weight, N the

Avogadro number, \bar{v} the partial specific volume of polymer, ρ_0 and η_0 the density and the viscosity of solvent, respectively, and S_0^0 the sedimentation coefficient for infinite dilution at 1 atm. Furthermore, $\kappa(A)$ is a function dependent upon a model chosen to describe the hydrodynamic interaction between the sedimenting molecules, and it monotonically decreases with increasing A . Here A is a thermodynamic interaction parameter defined by

$$A = (3n^2X)/(8\pi a^3) \quad (9)$$

where n is the number of segments per molecule, X the second virial coefficient for segment—segment interaction and, a the radius of the sphere.

According to the Stokes formula and the well-known Svedberg equation,¹⁶ the frictional expansion factor, α_f , is represented by

$$\alpha_f = a/a_\theta = (\eta_{0\theta}/\eta_0)(f/f_\theta) \\ = \{(1 - \bar{v}\rho_0)/(1 - \bar{v}_\theta\rho_{0\theta})\} \{(S_{0\theta}^0\eta_{0\theta})/(S_0^0\eta_0)\} \quad (10)$$

where f is the frictional coefficient and the subscript θ denotes the θ -temperature.

Using eq 10, eq 8 may be rewritten

$$k_s = (4/300)(1/N\pi)^2[(1 - \bar{v}_\theta\rho_{0\theta})/(6\eta_{0\theta}K_{s\theta})]^3 \\ \times [7.16 - \kappa(A)]M^{\frac{1}{2}}\alpha_f^3 \quad (11)$$

where $K_{s\theta}$ is a constant in the empirical relation between $S_{0\theta}^0$ and $M^{\frac{1}{2}}$, i.e., $S_{0\theta}^0 = K_{s\theta}M^{\frac{1}{2}}$.

According to eq 11, k_s is considered to be a function of both the segment—segment interaction parameter, A , defined in eq 9, and the frictional expansion factor, α_f . Since the segment—segment interaction can be related to the volume expansion by the two-parameter theory of dilute polymer solution, the authors attempt to represent k_s as a function of the expansion factor in the following discussion.

If the sedimenting particle is approximated by a soft sphere of uniform segment density, the radius of the sphere, a , may be taken to be equal to the root-mean-square radius of gyration $\langle s^2 \rangle^{\frac{1}{2}}$. Then A in eq 9 may be rewritten

$$A = (3n^2X)/(8\pi \langle s^2 \rangle_0^{3/2} \alpha^3) \quad (12)$$

where $\alpha = (\langle s^2 \rangle / \langle s^2 \rangle_0)^{\frac{1}{2}}$.

Here α is the expansion factor, and $\langle s^2 \rangle_0$ is the value of $\langle s^2 \rangle$ at the unperturbed state.

The term $n^2 X / \langle s^2 \rangle_0^{3/2}$ in eq 12 is proportional to the parameter of the volume exclusion, z . Consequently, one can rewrite eq 12 as follows

$$A = 3\pi^{1/2} (z/\alpha^3) \quad (13)$$

where $z = (n^2 X) (4\pi \langle s^2 \rangle_0)^{-3/2}$.

Various relations between z and α have been derived theoretically by several researchers. In this case, the following type of relationship may be employed.^{*,17}

$$\alpha^3 = 1 + 2z \quad (14)$$

Then, eq 13 becomes

$$A = 1.5\pi^{1/2} (1 - \alpha^{-3}) \quad (15)$$

Although any general relationship between the expansion factors has not been proposed, it seems reasonable to assume that $\alpha = \alpha_\xi = \alpha_\eta$ in the vicinity of θ -condition. In the following discussion, the authors employ α_η for the expansion factor mentioned above, because it is more accurately obtainable experimentally than the others. Further, the weight-average molecular weight is used for M in eq 11, because the molecular weight distribution of samples used was very narrow and the experimental accuracy in the measurement of \bar{M}_w is higher than that of \bar{M}_n .

Comparison with Experiment

When the $S_{0\theta}^0 - \bar{M}_w^{1/2}$ relations in the preceding section *i.e.*, eq 4 and 5, and the values for \bar{v}_θ , $\rho_{0\theta}$, and $\eta_{0\theta}$ listed in Table V are used for the calculation of the bracketed term in eq 11, the following equation is derived for each polymer—solvent system

$$k_s / \bar{M}_w^{1/2} = 2.29 \times 10^{-4} [7.16 - \kappa(A)] \alpha_\eta^3 \quad (16)$$

for poly(α -methylstyrene) and

$$k_s / \bar{M}_w^{1/2} = 2.87 \times 10^{-4} [7.16 - \kappa(A)] \alpha_\eta^3 \quad (17)$$

for polystyrene.

k_s at the θ -Condition. At the θ -condition, eq 11 shows that k_s is a linear function of $M^{1/2}$, because $\kappa(A)$ is a constant at $A=0$, although the value depends upon the model chosen to describe

* Strictly, when α is the expansion factor based on the radius of gyration, the relationship should be given by the form: $\alpha^3 = 1 + 1.91z$ (M. Fixman¹⁷). Here, eq 14 was employed for simplicity in further discussion, because z is small in the vicinity of θ -condition.

the hydrodynamic interaction.

In Figures 6 and 7, the values of k_s at the θ -temperature obtained in this work and reported by other investigators are plotted against $\bar{M}_w^{1/2}$. The authors' data for poly(α -methylstyrene) are seen to agree with those of Nagasawa, *et al.*⁷ and Kurata, *et al.*,⁸ although their measurements were made at 39.0°C as the θ -temperature. It is also seen that the authors' data for polystyrene

Table V. Characteristic values at the θ -temperature^a

System	\bar{v}_θ , ml/g	$\rho_{0\theta}$, g/ml	$\eta_{0\theta}$, g cm ⁻¹ sec ⁻¹
Poly(α -methylstyrene) in cyclohexane, 38.2°C	0.88 ₉	0.761 ₀	7.1 ₆ × 10 ⁻³
Polystyrene in cyclohexane, 35.0°C	0.92 ₈ ^b	0.764 ₀	7.6 ₀ × 10 ⁻³

^a \bar{v}_θ , partial specific volume of polymer; $\rho_{0\theta}$, density of solvent; $\eta_{0\theta}$, viscosity of solvent.

^b By Mandelkern, *et al.*¹⁰

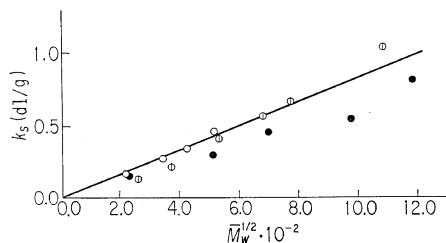


Figure 6. Plots of k_s vs. $\bar{M}_w^{1/2}$ for poly(α -methylstyrene) in cyclohexane at the θ -condition: ○, this work (38.2°); ○, Nagasawa, *et al.*⁷ (39.0°C); ●, Kurata, *et al.*⁸; solid line, obtained from the data in this work.

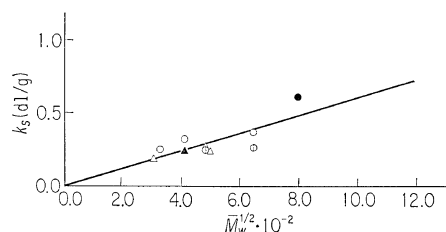


Figure 7. Plots of k_s vs. $\bar{M}_w^{1/2}$ for polystyrene in cyclohexane at the θ -temperature (35.0°C): ○, this work; ●, Wales, *et al.*¹⁴; △, Billick¹⁵; ○, Homma, *et al.*¹³; ▲, Billick⁵; solid line, obtained from the data both in this work and in the earlier reports.

satisfactorily agree with those earlier reports.^{5,13-15}

From these figures, it is concluded that k_s at the θ -state can be satisfactorily expressed as the linear function of $\bar{M}_w^{1/2}$. This result as well as those obtained by the other investigators^{5,7,8,12} fulfills the essential requirement of Pyun and Fixman theory at the θ -condition.⁴

The values for $\kappa(A)$ obtained from the slopes of the solid lines in these figures are 3.6 for poly(α -methylstyrene) and 5.0 for polystyrene, respectively.

k_s in the Vicinity of θ -Condition. The values of $k_s/\bar{M}_w^{1/2}$ obtained are plotted against α_η^3 in Figure 8 for poly(α -methylstyrene) and in Figure 9 for polystyrene.

It is found that $k_s/\bar{M}_w^{1/2}$ for each polymer increases monotonically with increasing α_η^3 and that the variation of $k_s/\bar{M}_w^{1/2}$ with α_η^3 appears to be expressed by a single line, regardless of the molecular weight of the sample.

In the same figures, the variations of $k_s/\bar{M}_w^{1/2}$ with α_η^3 calculated by eq 16 or 17 and 15 are shown by the dotted lines.

The dotted line is close to the experimental results in the region $\alpha_\eta^3 \approx 1$, and the discrepancy between calculated and experimental results increases with increasing α_η^3 . One might expect that another choice of the relationship between A and α_η would change the trend of the calculated curve. For example, one could take the equation.

$$A = 14.16(\alpha_\eta^2 - 1) \quad (18)$$

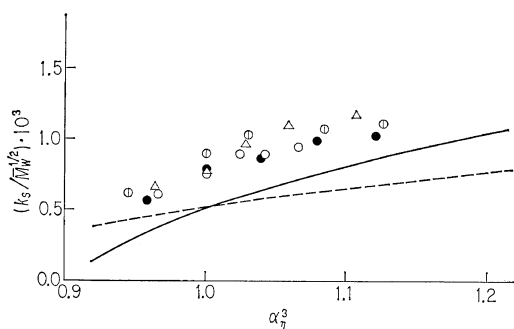


Figure 8. Variations of $k_s/\bar{M}_w^{1/2}$ with α_η^3 for poly(α -methylstyrene) in cyclohexane near the θ -point: \circ , PMS-6; \triangle , PMS-03; \bullet , PMS-227; \odot , PMS-10; dotted line, calculated through eq 16 by using eq 15; solid line, calculated through eq 16 by using eq 18.

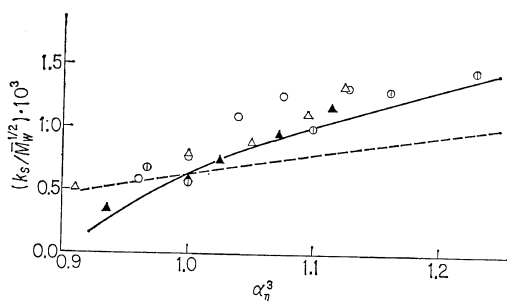


Figure 9. Variations of $k_s/\bar{M}_w^{1/2}$ with α_η^3 for polystyrene in cyclohexane near the θ -point: \circ , PS-9; \triangle , PS-16; \odot , PS-41; \blacktriangle , Billick⁵; dotted line, calculated by eq 17 by using eq 15; solid line, calculated by eq 17 with eq 18.

which was empirically estimated by Sakai¹⁸ in his investigation on Huggins' constant on the basis of the Peterson and Fixman theory.¹⁹ The calculated values of $k_s/\bar{M}_w^{1/2}$ by eq 18 are shown by the solid lines in Figures 8 and 9 for the respective polymers. Both figures indicate that the solid line fits the experimental data better than the dotted line. This result shows that the calculated $k_s/\bar{M}_w^{1/2}$ is considerably affected by the selection of the relationship between A and α_η .

Summarizing, the behavior of experimental $k_s/\bar{M}_w^{1/2}$ can be satisfactorily expressed by the Pyun and Fixman theory, though the selection of a more appropriate relationship between A and α_η is left for a further discussion.

Extension to Large Expansion of Polymer. In Figures 10 and 11, the solid and dotted lines show values of $k_s/\bar{M}_w^{1/2}$ for each polymer obtained by using eq 18 and 15, respectively. For comparison, the experimental data of $k_s/\bar{M}_w^{1/2}$ obtained in this work and those obtained by other investigators in various solvents^{2,5,7,20,21} are plotted.

It appears that the experimental data for each polymer can be represented by a single curve which tends to increase with increasing α_η^3 , regardless of the differences in solvent and in temperature, and that the solid lines based on eq 18 fit the experimental data satisfactorily.

It is concluded that the discrepancy between calculated and experimental results depends mainly on the relationship between A and α_η and that the present treatment of the Pyun and

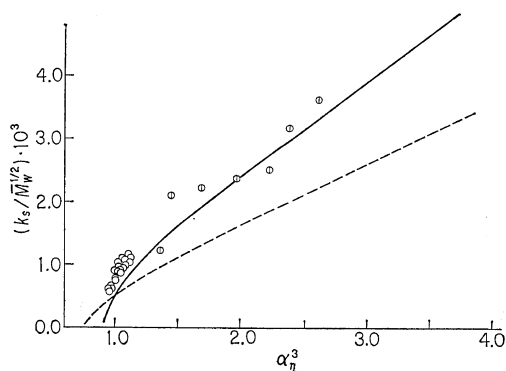


Figure 10. Variations of $k_s/\bar{M}_w^{1/2}$ with α_η^3 for poly(α -methylstyrene): \circ , in cyclohexane (this work); \odot , in toluene (Nagasawa, *et al.*⁷); solid line, calculated by eq 16 with eq 18; dotted line, calculated by eq 16 with eq 15.

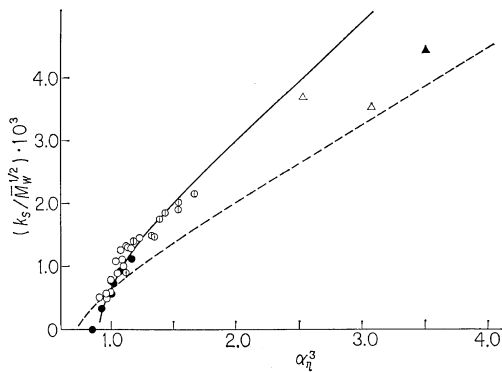


Figure 11. Variations of $k_s/\bar{M}_w^{1/2}$ with α_η^3 for polystyrene: \circ , in cyclohexane (this work); \bullet , in cyclohexane (Billick⁵); \odot , in butanone (Newman, *et al.*²⁰, Shick, *et al.*²¹, Van Holde, *et al.*²); \blacktriangle , in chloroform (Newman, *et al.*²⁰); \triangle , in toluene (Newman, *et al.*²⁰, Van Holde, *et al.*²); solid line, calculated eq 17 with eq 18; dotted line, calculated by eq 17 with eq 15.

Fixman theory may in effect be used for a further detailed investigation of k_s -behavior if an appropriate relationship between A and α_η can be found.

CONCLUSION

The requirement of the Pyun and Fixman theory at the θ -condition was fulfilled by the k_s -data obtained in this work and in earlier reports.

The k_s -behavior in the vicinity of θ -condition as well as in the region of larger expansion of

polymer was found to be satisfactorily expressed by the theory of Pyun and Fixman when an appropriate relationship between the segment—segment interaction parameter and the expansion factor was employed.

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