

# Prediction of Sedimentation Coefficients of Random Coil Polymers

C. M. KOK\* and ALFRED RUDIN, *Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1*

## Synopsis

The concentration dependence of the radius of gyration and the equivalent hydrodynamic radius of polymers in solution is described well by a model developed in earlier work. The calculated hydrodynamic volumes of solvated polymers are combined with the statistical mechanical calculations of Burgers for hard spheres to predict sedimentation coefficients at finite concentrations. The predicted values are in good agreement with experimental results.

## INTRODUCTION

Previous articles from this laboratory<sup>1-4</sup> have described a model which predicts the concentration dependence of the radius of gyration and the equivalent hydrodynamic radius of random coil polymers in solution. This theory has been applied to predict the concentration dependence of elution volumes in size exclusion chromatography.<sup>1,2,5</sup> When the calculated hydrodynamic volumes of solvated polymers are used with simple statistical-mechanical hard-sphere models, it is possible to obtain accurate predictions of turbidity and colligative properties of polymer solutions,<sup>6</sup> second virial coefficients,<sup>7</sup> and Flory-Huggins interaction parameters.<sup>8</sup> The input parameters needed are an average molecular weight of the polymer sample, its intrinsic viscosity in the solvent of interest, and its intrinsic viscosity under theta conditions.

The model used cannot possibly accord with all the properties of real polymer solutions, but it is able to predict a modest variety of phenomena with good accuracy without invoking adjustable parameters. This article reports the prediction of sedimentation coefficients by using the Rudin model<sup>1-4</sup> and the theoretical relation derived by Burgers<sup>9,10</sup> for hard spheres.

## THEORY

According to the Rudin model,<sup>1,2</sup> the radius of gyration of a polymer molecule in solution can be written as

$$R_G = \left[ \frac{3[\eta]M\phi_x}{9.3 \times 10^{24}\phi_x + 4\pi N_0 c([\eta] - [\eta]_\theta)} \right]^{1/3} \quad (1)$$

where  $M$  is the molecular weight of the polymer,  $[\eta]$  is the intrinsic viscosity of the polymer in the given solvent ( $\text{cm}^3/\text{g}$ ),  $[\eta]_\theta$  is the intrinsic viscosity under  $\theta$  conditions,  $N_0$  is the Avogadro's constant, and  $c$  is the concentration of polymer

\* On leave from Universiti Sains, Penang, Malaysia.

TABLE I  
 Mark-Houwink Constants of Polymers

Polymer	Solvent	Temp (°C)	$K \times 10^3$ (cm <sup>3</sup> /g)	$a$	Reference
Poly(styrene)	Toluene	25	8.48	0.748	14
	Methyl ethyl ketone	25	39.0	0.58	15
Poly( $\alpha$ -methyl styrene)	Toluene	25	7.06	0.744	16
Poly(isobutene)	Cyclohexane	30	27.6	0.69	12
Poly(methyl methacrylate)	Acetone	20	5.45	0.725	17
	Dioxane	25	6.54	0.75	17

(g/cm<sup>3</sup>). The dimensions of the solvated polymer molecules are assumed to shrink with increasing concentration from a limiting, maximum magnitude at infinite dilution to minimum sizes characteristic of the unperturbed,  $\theta$  state when the volume fraction of solute and included solvent has reached a critical value  $\phi_x$ . At zero concentration the second term in the denominator of eq. (1) vanishes, and this expression reduces to the Flory-Fox form for infinite dilution.<sup>11</sup> The coefficient of the first term in the denominator incorporates Flory's universal constant<sup>12</sup> with concentration units in g/cm<sup>3</sup>.

Recent experimental data<sup>3</sup> have shown that

$$R_H = 0.77 R_G \quad (2)$$

where  $R_H$  is the Stokes-Einstein hydrodynamic radius and  $R_G$  is the radius of gyration.

 TABLE II  
 Parameters Used in Calculations

Polymer	Solvent	Partial specific volume of polymer (cm <sup>3</sup> /g)	Density of solvent <sup>18</sup> (g/cm <sup>3</sup> )	Viscosity of solvent <sup>18,19</sup> (poise)
Polystyrene	Toluene	0.913 <sup>20</sup>	0.8669	0.0055
	Methyl ethyl ketone	0.954 <sup>20</sup>	0.805	0.0042
Poly( $\alpha$ -methyl styrene)	Toluene	0.913 <sup>a</sup>	0.8669	0.0055
Poly(isobutene)	Cyclohexane	1.091 <sup>21</sup>	0.779	0.0090
Poly(methyl methacrylate)	Acetone	0.798 <sup>18</sup>	0.7899	0.0031
Poly(methyl methacrylate)	Dioxane	0.818 <sup>21</sup>	1.027	0.0119

<sup>a</sup> Assumed same as polystyrene.

 TABLE III  
 $K_\theta$  and  $K_I$  of Polymers

Polymer	Temp (°C)	$K_\theta \times 10^3$ (cm <sup>3</sup> /g)	$K_I \times 10^3$ (cm <sup>3</sup> /g)
Poly(styrene)	34.5	84.6 <sup>22</sup>	4.9 <sup>23</sup>
Poly( $\alpha$ -methyl styrene)	34.5	73.0 <sup>16</sup>	4.9 <sup>a</sup>
Poly(isobutene)	25	130 <sup>24</sup>	10.09 <sup>b</sup>
Poly(methyl methacrylate)	45	48 <sup>25</sup>	4.85 <sup>26</sup>

<sup>a</sup> Assumed similar to poly(styrene).

<sup>b</sup> Calculated according to procedure of Ref. 4.

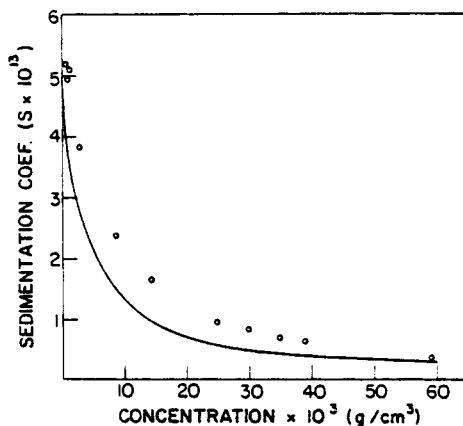


Fig. 1. Sedimentation constant as a function of concentration for  $1.8 \times 10^6$  molecular weight polystyrene in the  $\theta$  solvent, *trans*-decalin. The line is predicted and the points are experimental values from Ref. 27.

Sedimentation coefficients,  $S_0$ , at infinite dilution can be obtained from the Svedberg equation<sup>13</sup>:

$$S_0 = \frac{M(1 - \bar{v}\rho)}{N_0 6\pi\eta_0 R_H} \quad (3)$$

where  $\bar{v}$  is the partial specific volume of the polymer,  $\rho$  is the solution density, and  $\eta_0$  is the solvent viscosity.

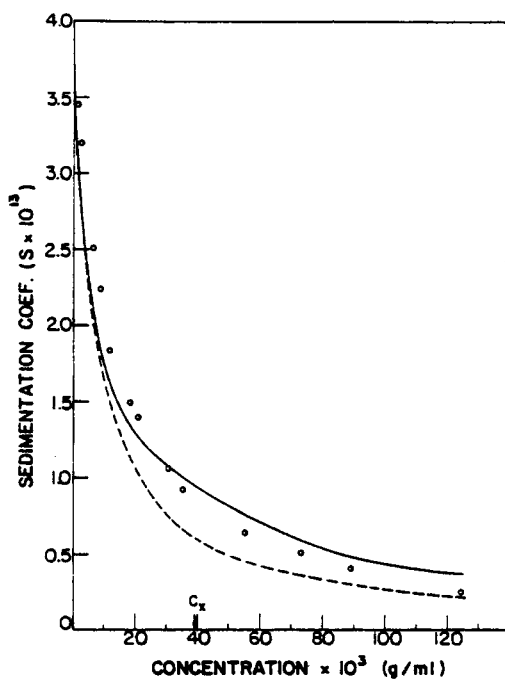


Fig. 2. Sedimentation constant of  $1.1 \times 10^6$  molecular weight polystyrene in toluene. The points are experimental. (—) Predicted by the present model; (---) calculated without allowance for concentration effects.

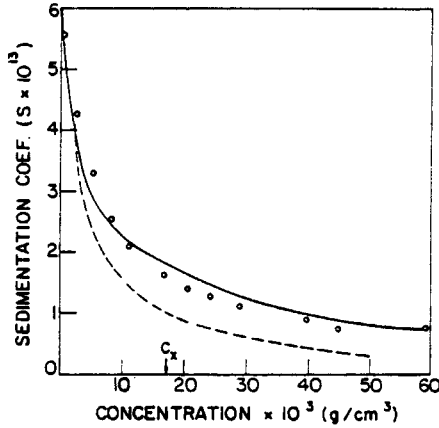


Fig. 3. Sedimentation constant of  $3.9 \times 10^5$  molecular weight polystyrene in toluene. Symbols are as in Figure 2.

The concentration dependence of sedimentation coefficients is generally written as

$$S = S_0(1 + k_1c)^{-1} \quad (4)$$

Using the hard spheres calculations of Burgers<sup>9</sup>

$$k_1 = (55/8)\phi \quad (5)$$

where  $\phi$  is the volume fraction of spheres. For a polymer in solution

$$\phi = N_0cV_h/M \quad (6)$$

where  $V_h$  is the hydrodynamic volume ( $\text{cm}^3/\text{molecule}$ ),  $c$  is in  $\text{cm}^3/\text{g}$ ,  $M$  in  $\text{g}/\text{mol}$ , and  $N_0$  in molecules/mol. Hence, for the hard sphere model

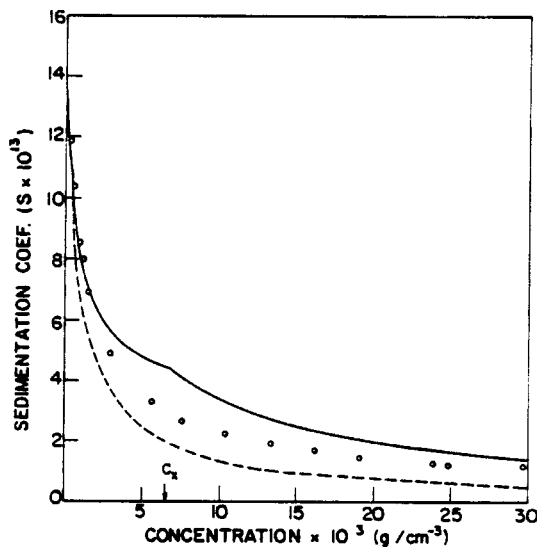


Fig. 4. Sedimentation constant of  $1.8 \times 10^6$  polystyrene in toluene. Symbols are as in Figure 2.

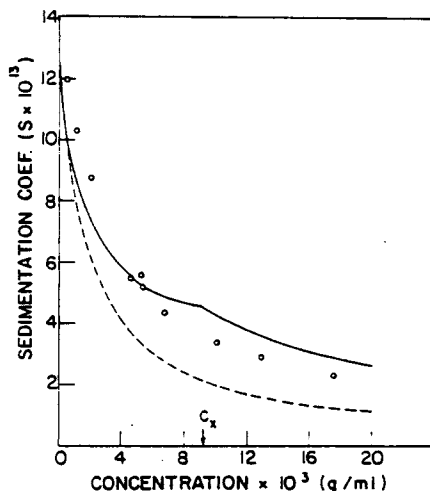


Fig. 5. Sedimentation constants as a function of concentration for  $1 \times 10^5$  molecular weight poly( $\alpha$ -methylstyrene) in toluene. The points are experimental.<sup>28</sup> (—) Predicted by the present model; (---) calculated without allowance for concentration effects.

$$k_1 = \frac{55}{8} \left( \frac{4\pi N_0 c R_H^3}{3M} \right) \quad (7)$$

Sedimentation coefficients at finite concentrations can be calculated using eqs. (1)–(4) and (7).

According to eq. (1),  $R_G$  decreases with concentration until the concentration,  $c_x$ , corresponding to the critical volume fraction  $\phi_x$ , is reached. This represents the boundary concentration at which the solvated polymer molecule has shrunk to its unperturbed volume. The value of  $c_x$  is given by<sup>1,2</sup>

$$c_x = \frac{9.3 \times 10^{24} \phi_x}{4\pi N_0 [\eta]_0} \quad (8)$$

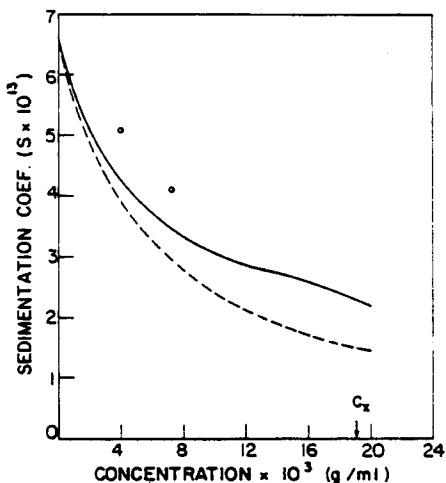


Fig. 6. Sedimentation constants for  $2.34 \times 10^5$  molecular weight poly( $\alpha$ -methylstyrene) in toluene. Symbols are as in Figure 5.

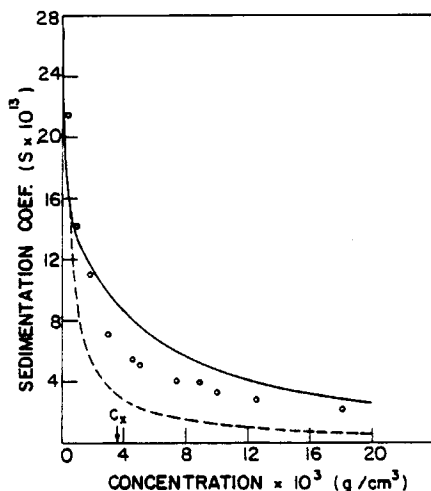


Fig. 7. Sedimentation constants for  $6 \times 10^6$  molecular weight poly( $\alpha$ -methylstyrene) in toluene. Symbols are as in Figure 5.

$\phi_x$  has recently been shown to be adequately represented by<sup>4</sup>

$$\phi_x = \frac{[\eta] - [\eta]_\theta}{[\eta]_I - [\eta]_\theta} \quad (9)$$

where  $[\eta]_I$  is the intrinsic viscosity for a hypothetical ideal solvent.

Further,

$$[\eta] = KM^a \quad (10)$$

$$[\eta]_\theta = K_\theta M^{1/2} \quad (11)$$

where  $K$ ,  $K_\theta$ , and  $a$  are the appropriate constants in the Mark-Houwink equations.  $[\eta]_I$  in eq. (9) can be calculated from  $K_\theta$  values or obtained from the lists of experimental values.<sup>4</sup>

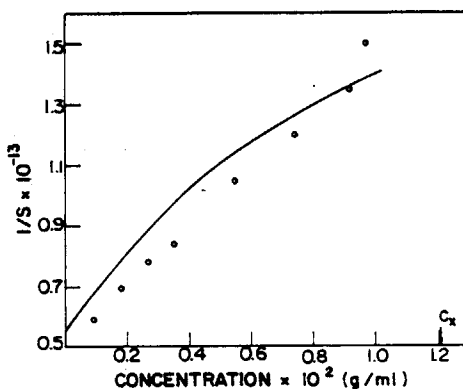


Fig. 8. Sedimentation constant of  $1.72 \times 10^5$  molecular weight polyisobutene in cyclohexane. The points are experimental,<sup>17</sup> and the line is predicted.

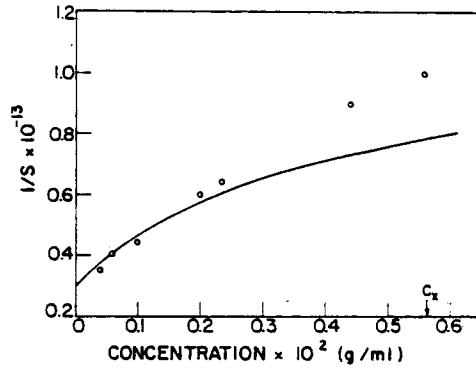


Fig. 9. Sedimentation constant of  $6.7 \times 10^5$  molecular weight polyisobutene in cyclohexane. Symbols are as in Figure 8.

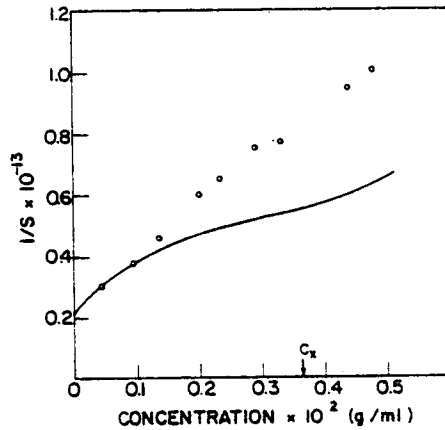


Fig. 10. Sedimentation constants of  $1.42 \times 10^6$  molecular weight polyisobutene in cyclohexane. Symbols are as in Figure 8.

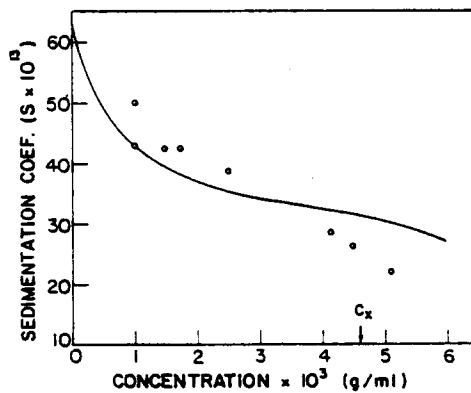


Fig. 11. Sedimentation constants of  $M_w 3.2 \times 10^6$  poly(methyl methacrylate) in acetone. The points are experimental,<sup>28</sup> and the line is predicted.

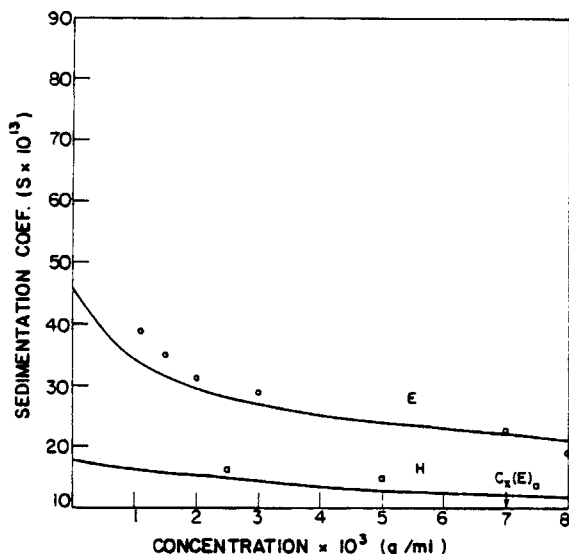


Fig. 12. Sedimentation constants for poly(methyl methacrylate) polymers in acetone. Symbols are as in Figure 11. (E)  $\bar{M}_w = 1.42 \times 10^6$ ; (H)  $\bar{M}_w = 1.48 \times 10^5$  ( $c_x$  of H =  $19.8 \times 10^{-3}$  g/cm<sup>3</sup>).

## RESULTS

The required input parameters for this application are  $[\eta]$ ,  $[\eta]_\theta$ , and  $[\eta]_I$ . These were obtained as described above. The constants and physical parameters used in this work are summarized in Tables I, II, and III.

Figures 1–4 show the recent sedimentation results of Nystrom and co-workers.<sup>27</sup> Under  $\theta$  conditions (Fig. 1),  $c_x$  and the second term in the denominator of eq. (1) are zero ( $[\eta] = [\eta]_\theta$ ). The predictions of the present model coincide with those of the infinite dilution Flory–Fox equation<sup>11</sup> in that case. The agreement with experiment is seen to be good, in this figure. Figures 2–4 compare predicted and experimental sedimentation constant–concentration relations for various polystyrenes in the good solvent, toluene. A better fit is provided by the theory of this article, even at concentrations well above  $c_x$ .

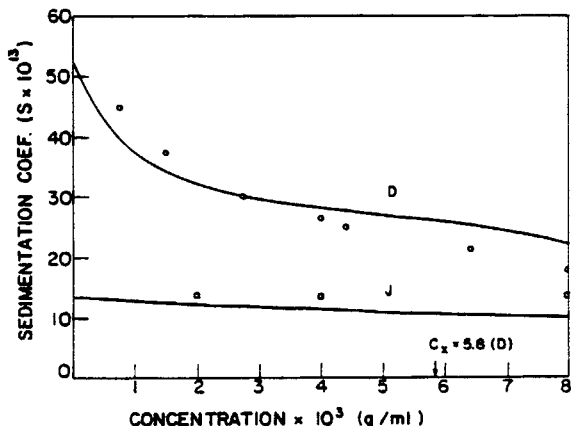


Fig. 13. Sedimentation constants for poly(methyl methacrylate) polymers in acetone. Symbols are as in Figure 11. (D)  $\bar{M}_w = 2.02 \times 10^6$ ; (J)  $\bar{M}_w = 7.72 \times 10^4$  ( $c_x$  of J =  $24.6 \times 10^{-3}$  g/cm<sup>3</sup>).



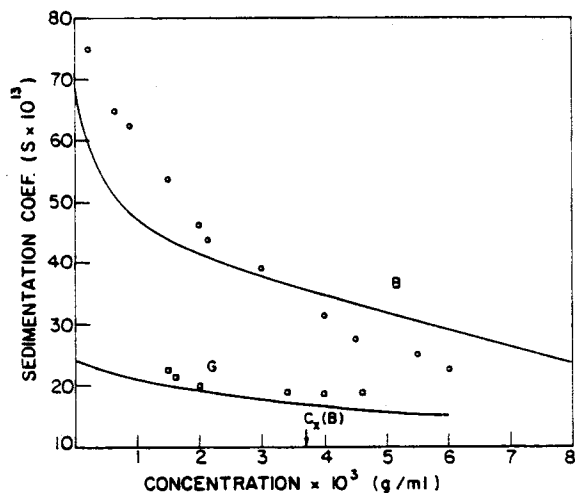


Fig. 14. Sedimentation constants of poly(methyl methacrylate) in acetone. Symbols are as in Figure 11. (B)  $\bar{M}_w = 4.59 \times 10^6$ ; (G)  $\bar{M}_w = 3.06 \times 10^5$  ( $c_x$  of G =  $14.6 \times 10^{-3}$  g/cm<sup>3</sup>).

Further tests of the model are shown in Figures 5–7, for poly( $\alpha$ -methylstyrene) samples in toluene.<sup>28</sup> Good agreement with experimental results is again observed.

Figures 8–10 compare our predicted values with the experimental data of Mandelkern and co-workers<sup>17</sup> for polyisobutene in cyclohexane. The experimental points here were read from published plots and are probably less reliable than those in the first two data sets quoted. The model gives good agreement with experimental values in this case for concentrations up to about  $0.5 c_x$ . The

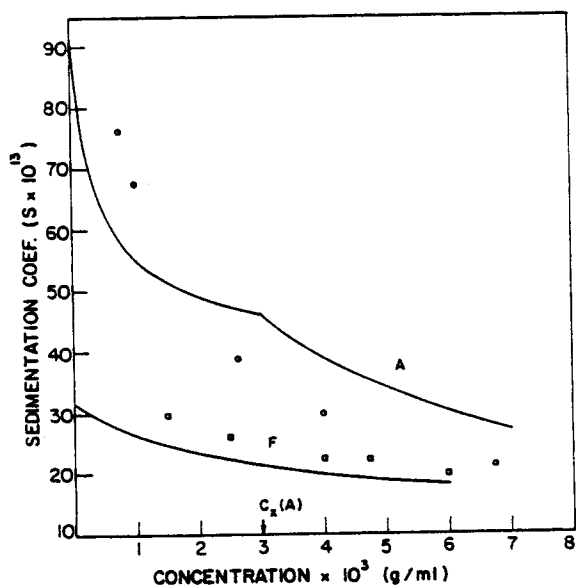


Fig. 15. Sedimentation constants for poly(methyl methacrylate) polymers in acetone. Symbols are as in Figure 11. (A)  $\bar{M}_w = 7.44 \times 10^6$ ; (F)  $\bar{M}_w = 6.11 \times 10^5$  ( $c_x$  of F =  $10.6 \times 10^{-3}$  g/cm<sup>3</sup>).

TABLE IV  
Comparison of Predicted and Experimental  $k_s$

Polymer	Solvent	Polymer mol wt $\times 10^{-5}$	Expt $k_s$ ( $\text{cm}^3/\text{g}$ )	Calcd $k_s$ ( $\text{cm}^3/\text{g}$ )	References
Poly(styrene)	Toluene (temp = 20°C)	13.0	400	366	29
		8.0	310	288	
		5.5	250	236	
		2.5	150	147	
	Methyl ethyl ketone (temp = 20°C)	13.0	230	296	229
		8.0	170	170	
		5.5	130	183	
		2.5	73	121	
Poly(isobutene)	Cyclohexane (temp = 20°C)	1.72	191	185	17
		6.72	510	450	
		14.2	836	764	
Poly(methyl methacrylate)	Acetone (20°C)	1.99	72	71	21
		13.0	224	210	
		65.0	614	603	
	Dioxane (25°C)	1.99	134	79.3	
		13.0	412	238	
		65.0	1040	712	

coincidence between predicted and experimental sedimentation coefficients is not as satisfactory at greater concentrations of higher molecular weight polyisobutenes.

The remaining figures are for poly(methyl methacrylate) polymers in acetone.<sup>26</sup> Here again the data points were taken from published plots and are probably less reliable than those in earlier examples. The model gives generally good agreement with experimental results.

## DISCUSSION

The theory presented here appears to be useful for predicting sedimentation coefficients. The agreement between estimated and experimental values is not close for the highest molecular weight specimens of polyisobutene and poly(methyl methacrylate), but these data may be less reliable than others because of experimental difficulties with sedimentation rates and molecular weight

TABLE V  
Comparison of Experimental  $k_s$  and Calculated  $k_s$  for PMMA/Dioxane

Mol wt $\times 10^{-6}$	Expt <sup>21</sup> concn limit $\times 10^{-3}$ g/mL	Expt $k_s$ ( $\text{cm}^3/\text{g}$ )	0.2 $c_x$ $\times 10^{-3}$ (g/mL)	Calcd $k_s$ ( $\text{cm}^3/\text{g}$ )
0.199	$\approx 4$	134	5.0	125
1.30	$\approx 4$	412	3.0	367
6.50	$\approx 1$	1040	1.1	979

measurements of such high molecular weight species when the studies in question were carried out some 30 years ago. The present model can generally be applied with confidence to a limit of  $c_x$  and even to higher concentrations in most cases.

An alternative way of expressing the concentration dependence of sedimentation rates is through the coefficient  $k_s$  in the expression

$$\frac{1}{S} = \frac{1}{S_0} [1 + k_s c] \quad (12)$$

It is a simple matter to apply the present model to calculate  $k_s$ . Sedimentation coefficients can be calculated up to  $0.5 c_x$ , and a least-squares line fitted to a plot of  $1/S$  vs.  $c$ . This procedure parallels that which was used recently to obtain second virial coefficients.<sup>7</sup> The  $0.5 c_x$  limit corresponds roughly to an upper concentration limit one would employ in an actual experiment. Results obtained using such a procedure are listed in Table IV. In most cases, good agreement with experimental data are obtained.

The coefficient  $k_s$  in reality depends on the concentration range, and is only a constant in very dilute solutions. One can obtain the best match between experimental and calculated results if the concentration limits of the two are similar. Table V shows this improvement for the last set of results in Table IV by using  $0.2 c_x$  as the concentration limit.

The present predictive method has been developed by considering polymer coils as equivalent in some respects to hard spheres. It is conceivable that flexible polymer coils can be represented thus to some extent. The procedure used here will probably not be adequate for rigid or semirigid polymers, however, and no claim is made for general applicability to all polymer solutions.

This work was supported by the Natural Sciences and Engineering Research Council of Canada.

## References

1. A. Rudin and R. A. Wagner, *J. Appl. Polym. Sci.*, **20**, 1483 (1976).
2. H. K. Mahabadi and A. Rudin, *Polym. J. (Jpn.)*, **11**, 123 (1979).
3. C. M. Kok and A. Rudin, *Makromol. Chem. Rapid Commun.*, **2**, 655 (1981).
4. C. M. Kok and A. Rudin, *Eur. Polym. J.*, **18**, 363 (1982).
5. C. M. Kok and A. Rudin, *Makromol. Chem.*, **182**, 2801 (1981).
6. C. M. Kok and A. Rudin, *J. Appl. Polym. Sci.*, **26**, 3575 (1981).
7. C. M. Kok and A. Rudin, *J. Appl. Polym. Sci.*, **26**, 3583 (1981).
8. C. M. Kok and A. Rudin, *J. Appl. Polym. Sci.*, **27**, 353 (1982).
9. J. M. Burgers, *Verh. K. Ned. Akad. Wet. (Sci. Sec.)*, **44**, 67, 1171 (1941); **45**, 9, 126 (1942).
10. M. E. Wales and K. E. van Holde, *J. Polym. Sci.*, **14**, 81 (1954).
11. P. J. Flory and T. G. Fox, Jr., *J. Am. Chem. Soc.*, **73**, 1904 (1951).
12. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953.
13. T. Svedberg and K. O. Pedersen, *The Ultracentrifuge*, Clarendon, Oxford, 1940, Johnson Reprint Corp., New York, 1959.
14. L. A. Papazian, *Polymer (London)*, **10**, 399 (1969).
15. P. Outer, C. I. Carr, and B. H. Zimm, *J. Chem. Phys.*, **18**, 830 (1950).
16. I. Noda, K. Mizutani, T. Kato, T. Fujimoto, and M. Nagasawa, *Macromolecules*, **3**, 787 (1970).
17. L. Mandelkern, W. R. Krigbaum, H. A. Scheraga, and P. J. Flory, *J. Chem. Phys.*, **20**, 1392 (1952).
18. J. Brandrup and E. H. Immergut, Eds., *Polymer Handbook*, Wiley, New York, 1975.

19. D. W. van Krevelen and P. J. Hoftyzer, *Properties of Polymers—Their Estimation and Correlation with Chemical Structure*, Elsevier, Amsterdam, 1976.
20. W. Heller and A. C. Thompson, *J. Colloid Sci.*, **6**, 57 (1951).
21. H. van Lutje and G. Meyerhoff, *Makromol. Chem.*, **68**, 180 (1963).
22. H. Inagaki, H. Suzuki, M. Fujii, and T. Matsuo, *J. Phys. Chem.*, **70**, 1718 (1966).
23. R. Endo and M. Takedu, *J. Polym. Sci.*, **56**, 28 (1962).
24. U. Bianchi, M. Dalpiaz, and E. Patrone, *Makromol. Chem.*, **80**, 112 (1964).
25. T. G. Fox, *Polymer (London)*, **3**, 111 (1962).
26. G. Meyerhoff and G. V. Schulz, *Makromol. Chem.*, **7**, 294 (1951).
27. B. Nystrom, B. Porsch, and L.-O. Sundelof, *Eur. Polym. J.*, **13**, 683, (1977).
28. P. F. Mijnlief and W. J. M. Jaspers, *Trans. Faraday Soc.*, **67**, 1837 (1971).
29. S. Newman and F. Eirich, *J. Colloid Sci.*, **5**, 541 (1950).

Received December 15, 1981

Accepted February 26, 1982