

Prediction of the Concentration Dependence of Diffusion Coefficients of Polymers in Solution

J. W. QIAN* and ALFRED RUDIN,[†] *Guelph-Waterloo Centre for Graduate Work in Chemistry, Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1*

Synopsis

The hydrodynamic volumes of solvated polymers shrink with increasing concentrations in solution until a concentration (c_x) is reached at which the effective dimensions are those of a Theta solvent. A simple model (Ref. 7) can be used to calculate the volume fraction of solvated polymer coils as a function of concentration. From this, the concentration dependence of diffusion coefficients can be estimated (Ref. 5). Calculated data are in very good agreement with experimental values except for some lower molecular weight polymers in poor solvents.

INTRODUCTION

Diffusion coefficients of polymers in solution are generally found to increase with higher concentrations. Exceptions to this relation are the results of King and co-workers¹ for low-molecular-weight polystyrenes in butanone-2 and various reports for polystyrenes in solution at or near Theta conditions.²⁻⁴ This article describes a method of predicting the concentration dependence of diffusion coefficients in non-Theta solvents.

We use the expression of Altenberger and Deutsch:⁵

$$D = D_o(1 + 2\phi) \quad (1)$$

where ϕ is the volume fraction of polymer in solution. As shown below, this very simple scheme provides good estimates of the concentration dependence of diffusion coefficients of polymers in various solvents. 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 intrinsic viscosities can be estimated in a straightforward fashion from the appropriate Mark-Houwink constants.

THEORY

According to the Rudin model,^{6,7} the radius of gyration of a polymer molecule in solution is given by:

$$R_G = \left(\frac{3[\eta]M\phi_x}{9.3 \times 10^{24}\phi_x + 4\pi N_o c([\eta] - [\eta]_\theta)} \right)^{1/3} \quad (2)$$

*On leave from Zhejiang University, Hangzhou, Peoples Republic of China.

[†]Address for correspondence.

where M is the molecular weight of the polymer, $[\eta]$ is the intrinsic viscosity of the polymer in the given solvent (cm^3/g), $[\eta]_\theta$ is the intrinsic viscosity under Theta conditions, N_0 is Avogadro's constant, and c is the concentration of polymer (g/cm^3). R_G is calculated to decrease with concentration until a concentration, c_x , corresponding to a critical volume fraction, ϕ_x , is reached. This represents the boundary concentration at which the solvated polymer molecules have shrunk to their unperturbed volumes. The value of c_x is given by:

$$c_x = \frac{9.3 \times 10^{24} \phi_x}{4\pi N_0 [\eta]_\theta} \quad (3)$$

The parameter ϕ_x has been shown to be adequately represented by⁸

$$\phi_x = \frac{[\eta] - [\eta]_\theta}{[\eta]_I - [\eta]_\theta} \quad (4)$$

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

The relationship between R_H and R_G is given by:⁹

$$R_H = 0.77 R_G \quad (5)$$

Obviously, the relationship between hydrodynamic volume (V_h) and radius of gyration, R_G is:

$$V_h = (0.77)^3 (4/3) \pi R_G^3 \quad (6)$$

The diffusion coefficient of a polymer at infinite dilution, R_{Ho} , can be expressed by the Stokes-Einstein equation:

$$D_o = \frac{\kappa T}{6\pi \eta_o R_{Ho}} \quad (7)$$

where κ is the Boltzmann constant, T is the absolute temperature, and η_o is the solvent viscosity. Since the Stokes-Einstein equation applies to infinite dilution conditions, the hydrodynamic radius, R_H , in Eq. (7) is subscripted with zero to indicate this restriction. Then, combining Eqs. (2) and (5) under zero concentration conditions, with Eq. (7) yields:

$$D_o = \frac{\kappa T}{6\pi \eta_o R_{Ho}} = \frac{\kappa T}{6\pi \eta_o (0.77)} \left(\frac{3.1 \times 10^{24}}{[\eta] M} \right)^{1/3} \quad (8)$$

The volume fraction, ϕ , of solvated polymer coils at mass concentration c is:

$$\phi = \frac{N_0 c V_h}{M} \quad (9)$$

TABLE I
 Constants and Parameters^a Used in Calculations

Polymer	Solvent	Temperature (°C)	K · 10 ³ (cm ³ /g)	Mark-Houwink constants a	Viscosity of solvent (η ₀) (poise)
Polystyrene	Butanone	25	39.0	0.58	0.004 ^h
Poly(α-methyl- styrene)	Toluene	25	7.81	0.73	0.0052
Polystyrene	THF	24	14.1 ^b	0.70 ^b	0.00462 ^b
Polystyrene	Toluene	21	4.16 ^c	0.788 ^c	0.0058 ^d
Polystyrene	Tetrachloro- methane	25	6.55 ^e	0.76 ^e	0.00888
Polystyrene	Cyclohexane	50	36.4	0.584	0.00525 ^f

^aAll data are from the *Polymer Handbook* (Ref. 12) except as noted. The K_θ and K_1 values of polystyrene are 0.0846 cm³/g (Ref. 13) and 0.0049 cm³/g (Ref. 14), respectively. K_θ and K_1 of poly(α-methylstyrene) are assumed similar to those of polystyrene (Ref. 15).

^bAssumed similar to Mark-Houwink constants at 25°C (Ref. 9).

^cAssumed similar to Mark-Houwink constants at 20°C.

^dObtained from interpolation of viscosities at 20°C and 25°C.

^eAssumed equal to K of PS-benzene at 25°C (Ref. 16).

^fObtained from extrapolation of viscosities at 20°C, 25°C, and 30°C.

^gRef. 16.

^hRef. 10.

Equations (1), (9), (6), (8), and (2) can be combined, then, to calculate diffusion coefficients as a function of concentration.

RESULTS AND DISCUSSION

The theory described above was used to predict diffusion coefficients for six polymer-solvent systems for which the appropriate physical constants could be located in the literature. These parameters are listed in Table I. Fortuitously, in five of the systems the solute is polystyrene.

Ford and co-workers¹⁰ have measured diffusion coefficients of polystyrene in 2-butanone solutions. At concentrations below about 3×10^{-3} g-cm⁻³ the diffusion coefficient was reported to be:

$$D = D_0(1 + k_d c) \quad (10)$$

with the constant k_d being molecular weight dependent. A polymer sample with molecular weight 6.7×10^5 received the most detailed study. A polystyrene with the same molecular weight has also been studied in the same solvent by King and co-workers,¹ and by Kok et al.¹¹ Figure 1 shows the data from these three sources along with the concentration dependence of D predicted as outlined above. The estimated values are in good agreement with experimental results, even at concentrations greater than c_x .

Ford and co-workers¹⁰ noted that k_d in Eq. (10) was positive for polymer molecular weights above $\sim 10^5$ and negative for lower molecular weight polystyrenes in 2-butanone. Equation (1) evidently does not allow for the

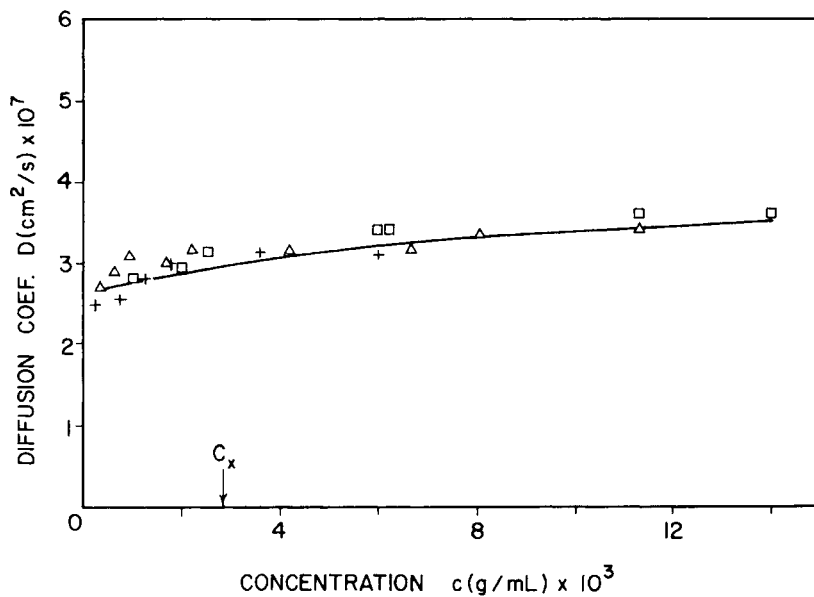


Fig. 1. Diffusion coefficients of 6.7×10^5 molecular weight polystyrene in 2-butanone at 25°C . The line is predicted. Data points are from the following references: 11 (\square), 10 (+), 1 (Δ).

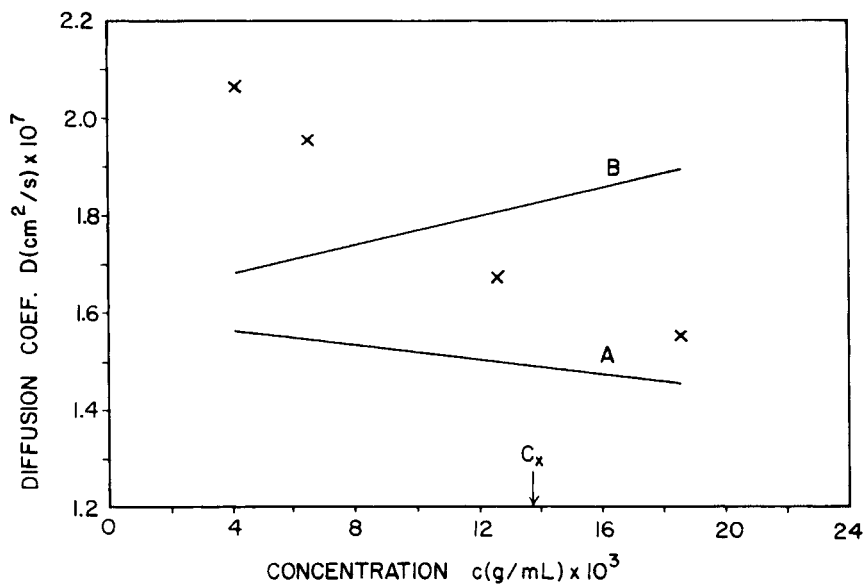


Fig. 2. Diffusion coefficients of 2.08×10^4 molecular weight polystyrene in 2-butanone at 25°C . Data points are from Ref. 1. Line A represents the experimental data of reference 10, while line B is predicted.

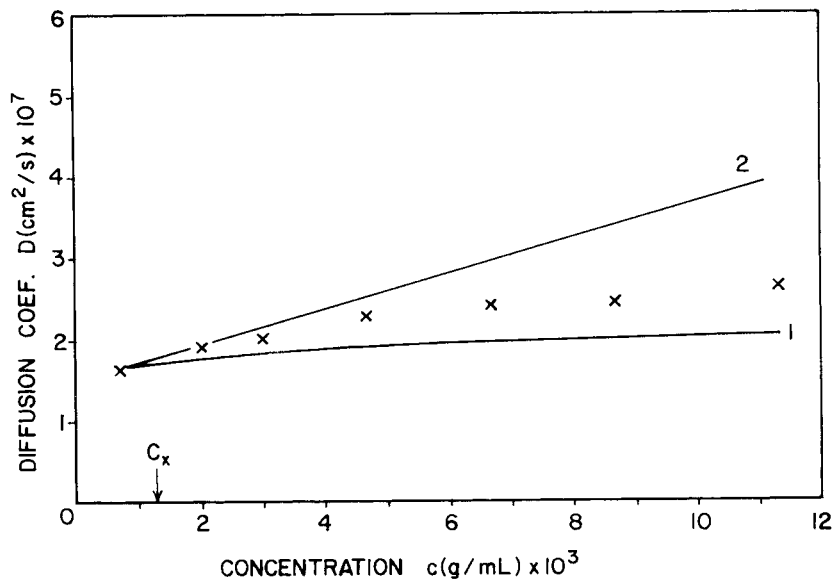


Fig. 3. Diffusion coefficient-concentration relation for 1.8×10^6 molecular weight polystyrene in 2-butanone at 25°C. Data are from Ref. 11 and line 1 is predicted from the present model, while line 2 is predicted from the equation of Ford and co-workers (Ref. 10).

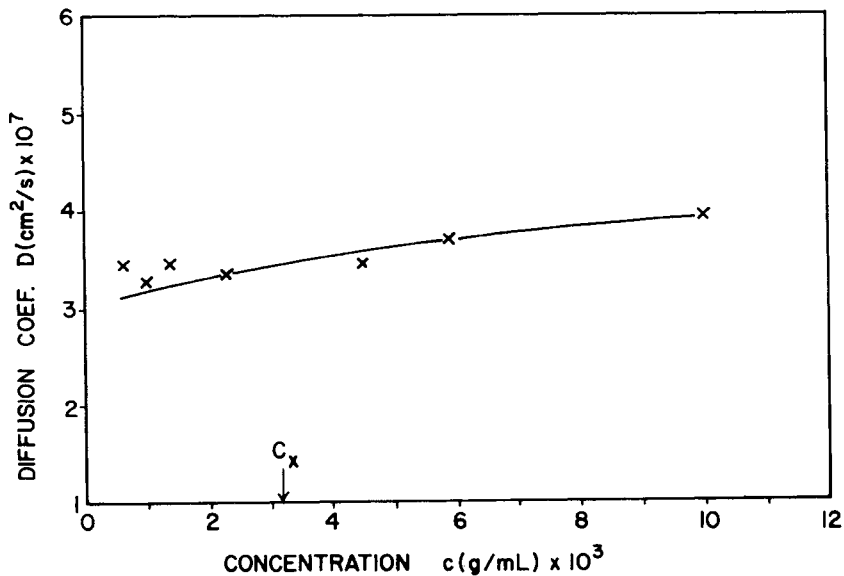


Fig. 4. Diffusion coefficient-concentration relation for 5.07×10^5 molecular weight polystyrene in 2-butanone at 25°C. The line is predicted and the data points are from Ref. 1.

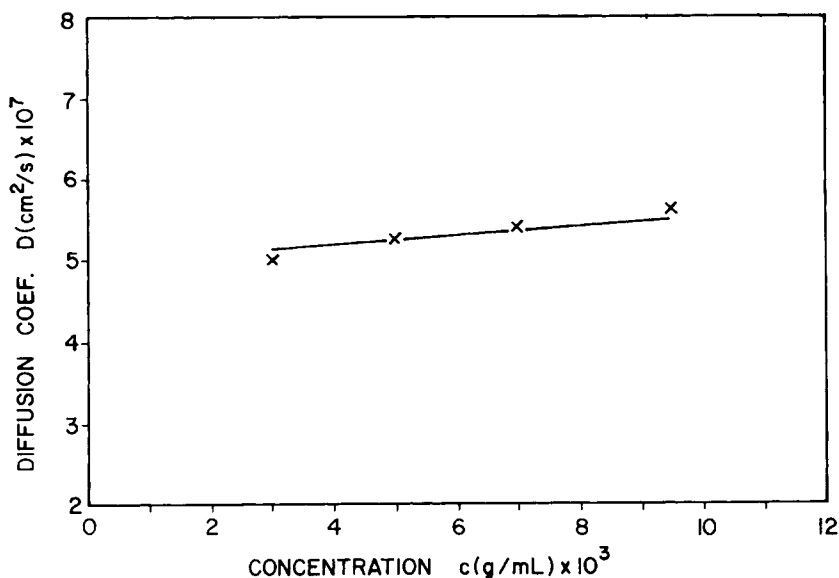


Fig. 5. Diffusion coefficient-concentration relation for poly(alpha-methyl styrene), molecular weight 1.69×10^5 , in toluene at 25°C . (Here $c_x = 0.015 \text{ g/mL}$). The line is predicted using 0.574 instead of 0.77 in Eq. (5) (Ref. 9) and the data points are from Ref. 18.

change of k_d from negative to positive values with increasing molecular weight. Other data of King and co-workers¹ and of Ford et al.¹⁰ are shown in Figure 2, along with the relation predicted by our model for the particular polymer (a 2.08×10^4 molecular weight polystyrene). The experimental values are in poor agreement. Nevertheless, both agree in showing decreasing diffusion coefficients with increasing concentrations, in contradiction to the predicted trend and to the behavior of similar polymers in other solvents (see below).

The agreement between estimated and experimental diffusion coefficients is much better for higher molecular weight polystyrenes in the same solvent, as shown in Figures 3 and 4. Good coincidence is also seen for poly(alpha-methylstyrene) in toluene, in Figure 5.

Figure 6 shows the behavior of a 2.04×10^4 molecular weight polystyrene in tetrahydrofuran. The predicted diffusion coefficient-concentration relation is in good agreement with observed values. A marked difference is seen between the behavior of this polymer in tetrahydrofuran (Fig. 6) and 2-butanone (Fig. 2).

Data for polystyrene in toluene (Fig. 7) and cyclohexane (at near-Theta conditions, Fig. 8) also are in good coincidence with the predicted relations.

Figures 3, 9, and 10 compare predicted values of D from the present model with the relation of Ford and co-workers.¹⁰ The latter authors used Eq. (10) in this connection. Values of D_0 and k_D in this equation are estimated from Eq. (11) and Eq. (12), respectively, according to hydrodynamic theory and the

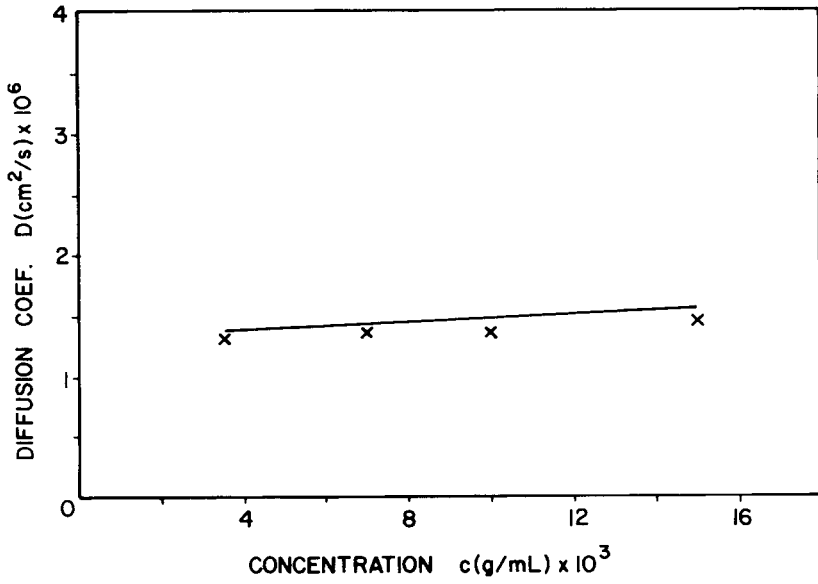


Fig. 6. Diffusion coefficients as a function of concentration for 2.04×10^4 molecular weight polystyrene in tetrahydrofuran at 24°C ; ($c_x = 0.158 \text{ g/mL}$). The line is predicted and the data points are from Ref. 19.

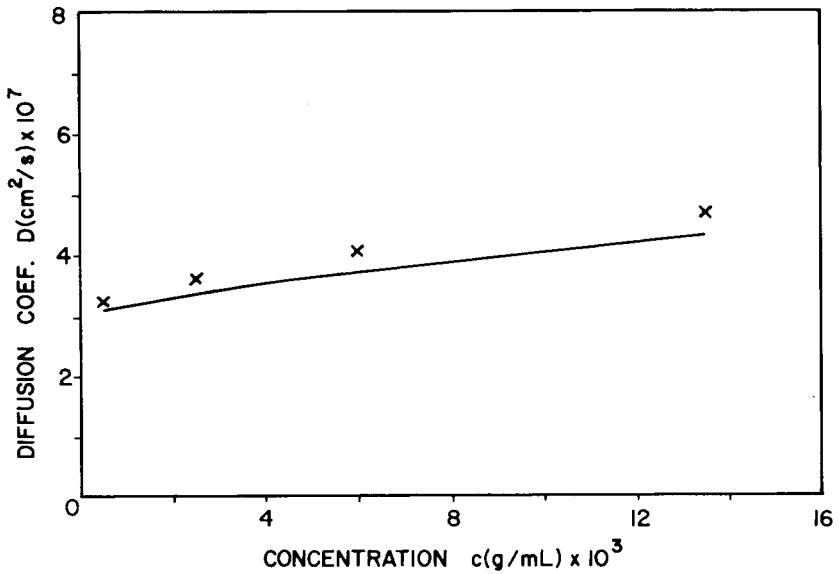


Fig. 7. Diffusion coefficients as a function of concentration for 2×10^5 molecular weight polystyrene in toluene at 21°C ($c_x = 0.017 \text{ g/mL}$). The line is predicted and the data points are from Ref. 20.

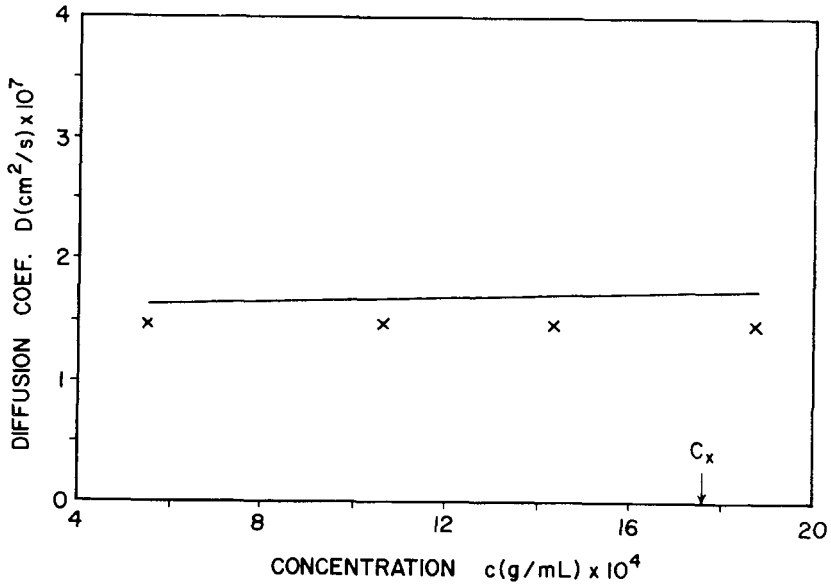


Fig. 8. Diffusion coefficient-concentration relation for 1.26×10^6 molecular weight polystyrene in cyclohexane at 50°C . The line is predicted and the data are from Ref. 3.

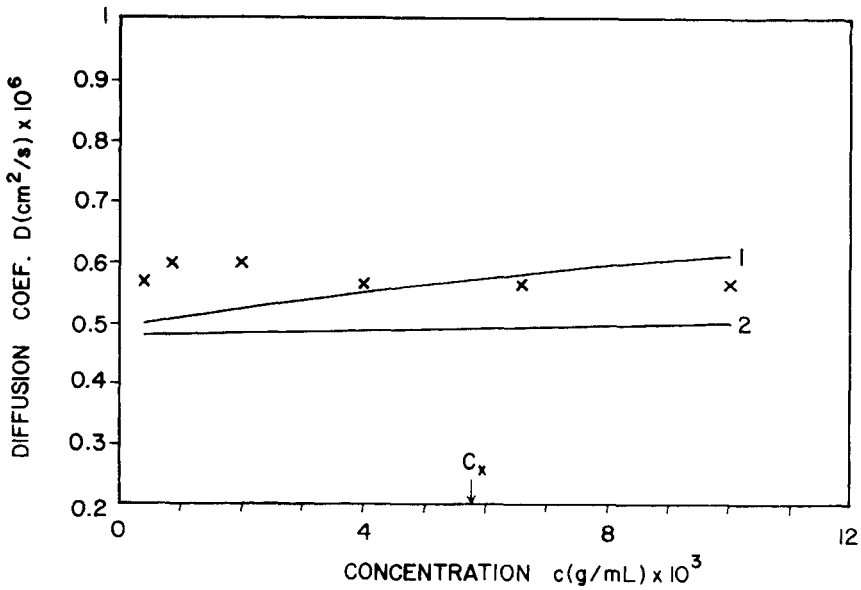


Fig. 9. Diffusion coefficient-concentration relation for 2.0×10^5 molecular weight polystyrene in 2-butanone at 25°C . Data points are from Ref. 1. Line 1 is predicted from present model, while line 2 is predicted from Ford's model.

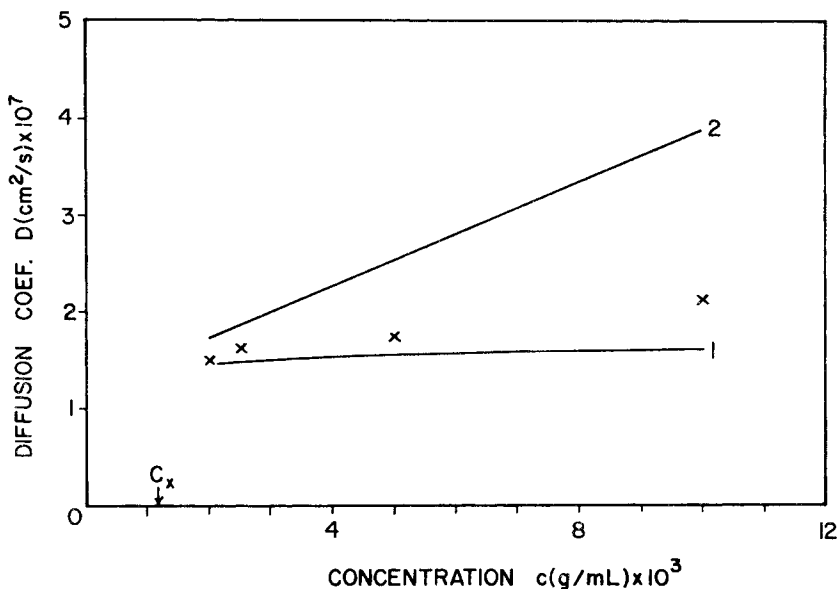


Fig. 10. Diffusion coefficient-concentration relation for 2.7×10^6 molecular weight polystyrene in 2-butanone at 25°C. Symbols are as in Figure 9.

Pyun-Fixman theory:²¹

$$D_o = k_D M^{-b} \tag{11}$$

where b is related to the exponent in the Mark-Houwink relation for the particular polymer-solvent system, k_D depends on b and the solvent viscosity, η_o , and

$$k_D = 2A_2 M + k'_j \tag{12}$$

Here

$$k'_j = \frac{4}{3} (k_f) \phi \left(\frac{M}{N_o \pi} \right)^2 \left(\frac{1 - v_o \rho_o}{6 \eta_o S_o} \right)^3$$

Ford and co-workers took 3.0 as the value of $(k_f) \phi$. The other symbols have their usual meanings.

It is of interest, further, to compare D_o values from Eq. (8) with experimental figures. These results, in Table II, shows generally very good agreement.

Most of the experimental data considered here cover only modest changes of D from D_o . In order to carry out a more critical evaluation of the theory, we have followed a referee's recommendation to compare experimental and predicted values of $(D - D_o)/D_o$ at various concentrations. These comparisons are shown in Table III. The coincidence appears to be satisfactory for the systems studied at polymer concentrations up to about 20 g/L. The predictive value of the present model is less satisfactory at higher concentrations and in Theta systems.

TABLE II
Comparison of Predicted and Experimental D_o Values

Polymer	Solvent	Polymer mol wt $\times 10^4$	Calcd. $D_o \times 10^7$ (cm^2/s)	Literature $D_o \times 10^7$ (cm^2/s)	Ref.
Polystyrene	Butanone (25°C)	67.0	2.60	2.42	10
		67.0	2.60	2.76	
		180.0	1.54	1.47	11
		20.0	4.92	4.92	
		67.0	2.60	2.9 ± 0.1	1
		270.0	1.25	1.30 ± 0.03	
		50.7	3.02	3.30 ± 0.1	
		39.2	3.46	3.95 ± 0.15	
		20.0	4.93	5.95 ± 0.1	
		2.08	—	—	
Poly(α -methyl- styrene)	Toluene (25°C)	350	1.07	~ 1.1	17
		110	1.66	1.61 ± 0.02	
		45.7	2.77	2.77 ± 0.02	18
		16.9	4.91	4.76 ± 0.07	
Polystyrene	Tetrahydrofuran (24°C)	8.37	7.36	6.1 ± 0.02	
		180	0.98	1.01	
		86	1.52	1.59	
		41.1	2.34	2.35	
		16	4.06	3.99	19
Polystyrene	Toluene (21°C)	9.72	5.48	5.43	
		5.1	7.96	7.65	
		2.04	13.3	12.7	
		$\sim 25^a$	2.65	~ 2.2	
		20	3.03	3.25 ± 0.1	20
		20	3.03	$\sim 3.4^b$	
		11.1	4.30	4.25 ± 0.1	
Polystyrene	Tetrachloro- methane (CCl_4 , 25°C)	11.0	4.26	4.50	4
		500	2.95	~ 3.0	17
Polystyrene	Cyclohexane (50°C)	350	3.64	~ 4.5	
		126	1.54	~ 1.43	3

^aBroad molecular weight distribution sample.

^bExperimental value at high concentration.

TABLE III
Comparison of Predicted and Experimental Values of $\frac{D - D_o}{D_o}$

Polymer	Solvent/Temp (°C)	Mol. Wt. $\times 10^{-4}$ (g/mol)	$C \times 10^3$ (g/mL)	$\left[\frac{D - D_o}{D_o} \right]_{(q)}$ $\times 100$ pred.	$\left[\frac{D - D_o}{D_o} \right]_{(q)}$ $\times 100$ Exp.	Ref.
poly (α -methyl- styrene)	Toluene(25)	8.37	3.90	3.48	3.28	18
			7.90	6.68	6.56	
			1.10	8.93	9.84	
			1.60	12.22	18.03	
polystyrene	Butanone (25)	67.0	1.0	6.16	2.17	11
			2.0	11.08	6.88	
			2.5	13.18	13.77	
			6.0	23.68	23.55	
			6.25	24.23	23.91	
			11.3	32.30	30.43	
			14.0	35.09	30.43	
			0.2	1.68	1.24	10
			0.75	4.75	5.37	
			1.25	7.49	15.70	
			1.75	9.94	23.97	
			3.6	17.17	29.34	
			6.0	23.68	28.10	
			20.0	2.0	6.39	7.72
3.0	9.25	13.82				

TABLE III (Continued from the previous page.)

Polymer	Solvent/Temp (°C)	Mol. Wt. $\times 10^{-4}$ (g/mol)	$C \times 10^3$ (g/mL)	$\left[\frac{D - D_o}{D_o} \right]_{(\varphi)}$	$\times 100$ pred.	$\left[\frac{D - D_o}{D_o} \right]_{(\varphi)}$	$\times 100$ Exp.	Ref.
			4.0		11.92		26.02	
			5.67		16.00		23.98	
			6.0		16.76		17.48	
			7.67		20.36		17.89	
			8.67		22.35		21.95	
			12.0		28.21		36.18	
			14.7		32.22		41.26	
			16.0		34.02		25.00	
polystyrene	THF(24)	41.1	0.8		6.28		2.13	19
			1.5		10.67		10.64	
			3.0		17.76		19.15	
			6.0		26.59		48.9	
		9.72	1.0		3.18		3.68	
			1.5		4.74		4.97	
			3.0		9.25		7.74	
			6.0		17.61		19.71	
			10.6		29.01		27.07	
			12.0		32.1		30.76	
			16.5		41.54		45.49	
		5.10	2.5		5.07		0.79	
			5.0		9.56		9.80	
			10.0		19.20		14.38	
			12.5		23.58		18.30	
			15.0		27.80		26.14	
			20.0		25.83		37.30	
		2.04	3.5		3.79		2.36	
			7.0		7.55		5.91	
			10.0		10.74		5.91	
			15.0		16.01		12.60	
polystyrene	Toluene(21)	20.0	0.50		2.28		0.31	20
			2.5		10.60		10.77	
			6.0		22.64		24.62	
			13.5		41.24		43.08	
		20.0	2.75		11.56		2.94	
			6.25		23.40		20.59	
			12.5		39.18		41.76	
			25.0		59.12		71.47	
			50.0		79.28		135.3	
			100		95.58		202.9	
		11.1	2.75		7.61		7.98	
			6.0		15.63		16.20	
			15.0		33.57		38.50	
	Toluene(25)	11.0	0.49		1.80		1.56	4
			0.494		1.82		1.78	
			4.9		16.61		14.44	
			9.9		30.68		31.78	
			20.1		53.16		57.11	
			40.1		82.38		101.8	
			49.8		92.32		123.6	
			69.9		107.8		154.4	
			85.6		116.7		174.4	
			100.6		123.4		195.1	
			121.0		130.6		213.8	
polystyrene	Cyclohexane(50)	1.260	0.55		4.84		14.0	3
			1.06		8.48		14.0	
	(near θ temp.)		1.44		10.73		14.0	
			1.88		13.03		14.0	

CONCLUSIONS

In this instance, reasonable predictions of diffusion coefficients of polymers in solution have been obtained by treating the solvated macromolecules as hard spheres,⁵ along with a model that allows for variation of the hypothetical hard sphere dimensions with concentration.^{6,7} Similarly, hard sphere calculations have been shown to provide good predictions of osmotic pressures, turbidities, and second virial coefficients,²² Flory-Huggins interaction parameters,²³ solubility parameters²⁴ and sedimentation coefficients.¹⁵ It is surprising that such simple ideas are useful to predict the behavior of complex systems. The model described cannot possibly reflect real polymer solutions in all respects, but no other more complicated theory yet matches the predictive ability of the present concepts.

The authors thank the Natural Sciences and Engineering Research Council of Canada and Directorate of Pao Yu-Kong and Pao Zao-Long Scholarship for financial support of this research.

References

1. T. A. King, A. Knox, and J. D. G. McAdam, *Polymer (London)*, **14**, 293 (1973).
2. T. A. King, A. Knox, W. I. Lee, and J. D. G. McAdam, *Polymer (London)*, **14**, 151 (1973).
3. M. J. Pritchard and D. Caroline, *Macromolecules*, **14**, 424 (1981).
4. J. Roots, B. Nystrom, and L. O. Sundelof, *Polymer (London)*, **20**, 337 (1979).
5. A. R. Altenberger and J. M. Deutsch, *J. Chem. Phys.*, **59**, 894 (1972).
6. C. M. Kok and A. Rudin, *J. Macromol. Sci. Revs. Macromol. Chem. Phys.*, **C24**, 49 (1984).
7. A. Rudin and R. A. Wagner, *J. Appl. Polym. Sci.*, **20**, 1483 (1976).
8. C. M. Kok and A. Rudin, *Eur. Polym. J.*, **18**, 363 (1982).
9. C. M. Kok and A. Rudin, *Makromol. Chem. Rapid Commun.*, **2**, 655 (1981).
10. N. C. Ford, F. E. Karasz, and J. E. M. Owen, *Disc. Faraday Soc.*, **49**, 228 (1970).
11. C. M. Kok, F. R. Hallett, and A. Rudin, *Eur. Polym. J.*, **21**, 33 (1985).
12. J. Brandup and G. H. Immergut (Eds.), *Polymer Handbook*, Wiley, New York, 1975.
13. H. Inagaki and H. Suzuki, *J. Phys. Chem.*, **70**, 1718 (1966).
14. R. Endo and M. Takedu, *J. Polym. Sci.*, **56**, 28 (1962).
15. C. M. Kok and A. Rudin, *J. Appl. Polym. Sci.*, **27**, 3357 (1982).
16. A. Dondos and V. Skordilis, *J. Polym. Sci., Polym. Phys. Ed.*, **23**, 615 (1985).
17. V. N. Tvetskov and S. I. Klemin, *J. Polym. Sci.*, **30**, 187 (1958).
18. J. C. Selsler, *Macromolecules*, **14**, 346 (1981).
19. W. Mandema and H. Zeldeurust, *Polymer (London)*, **18**, 835 (1977).
20. P. N. Prusey and J. M. Vaughn, *J. Chem. Soc. Faraday Trans. II*, **70**, 1696 (1974).
21. C. W. Pyun and M. Fixman, *J. Chem. Phys.*, **41**, 937 (1964).
22. C. M. Kok and A. Rudin, *J. Appl. Polym. Sci.*, **26**, 3583 (1981).
23. C. M. Kok and A. Rudin, *J. Appl. Polym. Sci.*, **27**, 353 (1982).
24. C. M. Kok and A. Rudin, *J. Coatings Technol.*, **55** (704), 57 (1983).

Received March 19, 1988

Accepted March 22, 1988