ELSEVIER

Polymer 43 (2002) 1623–1630

polymer

www.elsevier.com/locate/polymer

Modeling solute diffusion in aqueous polymer solutions

Brian Amsden

Department of Chemical Engineering, Queen's University, Kingston, Ont., Canada, K7L 3N6

Received 2 July 2001; received in revised form 23 October 2001; accepted 25 October 2001

Abstract

There are numerous models describing solute diffusion in polymer solutions. An analysis of these models demonstrates that none can provide a consistent explanation of the phenomenon observed for solutes that can be modeled as essentially solid spheres. For this reason, a new model based on a physical obstruction approach is presented. In this model, solute movement in the presence of polymer chains is assumed to be governed by the probability of the solute molecule encountering a series of openings between the chains larger than its hydrodynamic radius. The model is tested against data taken from the literature for a series of polymer solutions and solute probes and found to provide good agreement to the effects of solute size, polymer concentration, and polymer flexibility. © 2002 Published by Elsevier Science Ltd.

Keywords: Obstruction-scaling; Model; Solute diffusion

1. Introduction

The study of the diffusion of small molecules, globular proteins and colloidal particles in aqueous polymer solutions is important in gaining an understanding of drug diffusion in biological fluids and in the release of drugs from drug formulations such as tablets. To study these areas more effectively, it would be useful to have at hand a mathematical expression capable of accurately predicting solute diffusivities. Any such model will have to accurately reflect the experimentally observed dependence of solute diffusivity on solute size, polymer properties and polymer concentration.

There have been numerous attempts at providing predictions for solute diffusivity within polymer solutions and gels. Mechanisms used as a basis include enhanced hydrodynamic drag on the solute molecule [1–3], energy barriers to solute jumps [4], and physical obstruction due to the presence of the polymer chains [5–7]. None of these models is successful at explaining all the experimental observations.

In this paper, an obstruction-scaling model originally developed for predicting solute diffusion in gels is demonstrated to be applicable to describing solute diffusion in semi-dilute polymer solutions. The discussion begins with a description of the limitations of existing models when compared to experimental data taken from the literature. This discussion leads to the development of the obstruction-scaling model. The model is compared to literature data to demonstrate its applicability, and its underlying assumptions and limitations are discussed.

1.1. Literature findings

Before discussing the existing models, it is useful to examine characteristic experimental results. All of the models to be discussed have in common the assumption that the solute molecule is a solid sphere, and so only data in which the solute can be considered essentially Brownian will be examined. Data of solute diffusion in aqueous, non-ionic polymer solutions were collected from the literature. These literature sources, the polymers comprising the solution, and the method used to determine diffusivity are listed in Table 1. As none of the models considered account for solute–polymer interactions, data in which these interactions were likely were not used.

The physical properties of the polymers are listed in Table 2 along with the reference from which the values were obtained. The polymer chain radius, r_f, listed in Table 2 was calculated from the following relationship [7],

$$r_f = \left(\frac{M_m v}{l\pi N_A}\right)^{\frac{1}{2}} + r_w \tag{1}$$

in which l is the length of the monomer unit, M_m is the molecular weight of the monomer, v is the specific volume of the polymer, r_w is the radius of a water molecule and N_A is Avogadro's number. The radius of one water molecule is

---

E-mail address: amsden@chee.queensu.ca (B. Amsden).

0032-3861/02/$ - see front matter © 2002 Published by Elsevier Science Ltd.
PII: S0032-3861(01)00749-2

Table 1
Polymer solutions examined and the data author (abbreviations: PVA = poly(vinyl alcohol); HPC = hydroxypropyl cellulose; NIPAAM = poly(*N*-isopropylacrylamide))

Polymer	Method	Reference
PVA	Pulsed-gradient spin echo NMR	[19]
Dextran	Holographic interferometry	[11]
HPC	Fluorescent photobleaching recovery	[14]
NIPAAM	Pulsed-gradient spin echo NMR	[16]

added to account for the hydration sheath surrounding the polymer backbone chain.

The solutes used in these studies and their radii are listed in Table 3. These radii were calculated using the Stokes–Einstein expression,

$$r_s = \frac{k_B T}{f \pi \eta D_0} \tag{2}$$

in which k_B is Boltzmann's constant, T is temperature, η is solvent viscosity at T, and f is 4 for solutes whose size approach that of the solvent (i.e. water) and 6 for solutes greater in size than water [8]. The radius of the water molecule was chosen as 1.85 Å which is an average of the three most consistent values listed in Table 3.

The influence of polymer concentration on solute diffusivity is shown in Fig. 1 while the influence of solute hydrodynamic radius is given in Fig. 2. In these figures, the diffusivity has been normalized with respect to the diffusivity of the solute in an aqueous medium alone under the same temperature condition. Fig. 1 shows that there is an exponential decrease in diffusivity as the polymer concentration increases, as has been well established in the literature. Fig. 2, which shows the influence of solute radius in a given polymer solution, clearly demonstrates that a Gaussian, or $D/D_0 = \exp(-Kr_s^2)$ where K is a constant, dependence exists. A successful model of the diffusion process must therefore capture both of these effects.

Table 3
Solutes and their hydrodynamic radius (abbreviations: EG-Me = ethylene glycol methyl ether; EG-Me$_2$ = ethylene glycol dimethyl ether; EG-*t*BuMe = ethylene glycol *tert*-butyl methyl ether; 18-crown-6 = crown ether; PEG = poly(ethylene glycol); BSA = bovine serum albumin; FD-# = FITC-dextran and the number following indicates the molecular weight of the dextran in kDa)

Solute	D_0 ($\times 10^6$ cm^2/s)	T	r_s (Å)	Reference
Water	1.72	25	2.13	[16]
	1.95	23	1.78	[31]
	2.22	30	1.88	[25]
	2.30	30	1.82	[32]
EG-Me	7.88	25	3.07	[19]
EG-Me$_2$	7.56	25	3.24	
EG-*t*BuMe	5.58	25	4.38	
18-crown-6	4.37	25	5.54	
PEG 326	4.9	25	4.8	[33]
PEG 1118	2.8	25	8.9	
PEG 2834	1.8	25	13.8	
PEG 3978	1.5	25	15.8	
PEG 400	3.3	23	7.0	[35]
PEG 600	1.86	23	12.5	
PEG 1000	1.66	23	14.0	
PEG 1500	1.13	23	20.6	
PEG 2000	1.07	23	22.6	
PEG 4000	0.96	23	24.3	
BSA	0.60	20	36.3	[34]
γ-Globulin	0.40	20	53.0	
FD-9	0.154	30	18.1	[14]
FD-20	0.0996	30	27.8	
FD-70	0.048	30	58.0	
FD-150	0.0315	30	88.5	
FD-2000	0.0155	30	179.0	

1.2. Review of scaling theory

Another feature of many of the models being considered is that they invoke polymer solution scaling relationships to describe the average distance between interacting polymer chains in solution, i.e. the mesh size, ξ. The average mesh size is a function of the polymer physical properties, its affinity for the solvent, and the concentration of polymer in the solution. All of these factors are incorporated into

Table 2
Physical properties of polymers examined

Polymer	M_m (g/mol)	v (cm^3/g)[a]	l (Å)[b]	a (Å)	r_f (Å)[c]	χ	C
PVA	44	0.765	2.51	1.54	6.40	0.494	8.5
Dextran	162	0.625	5.14	5.14	6.92	0.473	9.0
NIPAAM	113	0.896	2.51	1.54	8.32	0.510[d]	10.6[e]
HPC	336	0.8057	5.14	5.14	7.12	0.480[f]	52.3[g]

[a] From Ref. [26].

[b] Calculated from bond angles and bond lengths, except dextran for which the value for alginate was assumed (see Ref. [21]).

[c] Calculated using Eq. (1).

[d] From Ref. [27].

[e] From Ref. [28].

[f] From Ref. [29].

[g] Calculated from persistence length given in Ref. [30].

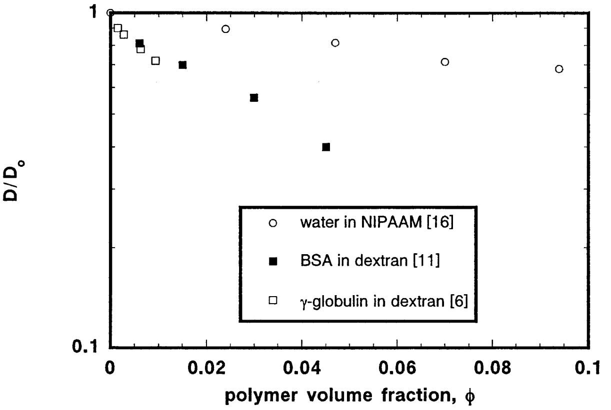

Fig. 1. Effect of polymer volume fraction on solute diffusivity in aqueous polymer solutions.

scaling theory. Therefore, in order to discuss the models effectively, a brief review of semi-dilute solution scaling relationships is necessary.

The solution behavior of a polymer is dictated to a large extent by its concentration. Schaefer, using thermodynamic arguments based on excluded volume effects, defines concentration crossover regimes wherein the semi-dilute polymer solution behavior changes from good to marginal to theta solvent conditions [9]. In the good solvent regime, the assumptions of scaling theory are valid, and ξ is given by,

$$\xi \sim a\phi^{-\frac{3}{4}}C^{-\frac{1}{4}}(1-2\chi)^{-\frac{1}{4}} \tag{3}$$

in which a is the effective bond length, ϕ is the polymer volume fraction in solution, and C and χ are the polymer characteristic ratio and interaction parameter, respectively. Eq. (3) holds until the marginal regime is reached. The polymer volume fraction at which this occurs is,

$$\tilde{\phi} = \frac{3}{4\pi}\frac{(1-2\chi)}{\left(\frac{C}{6}\right)^3} \tag{4}$$

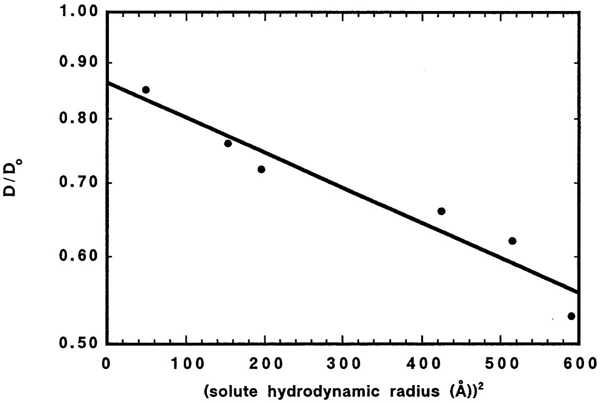

Fig. 2. Effect of solute radius on its diffusivity in aqueous polymer solutions. Data taken from Masaro et al. for PEGs diffusing in PVA [16].

Table 4
Crossover polymer concentrations defining solvent regimes and applicable scaling parameter value, ν, based on concentration range of polymer solution in study

Polymer	$\tilde{\phi}$	ϕ^+	ν
PVA	0.001	0.012	1.0
Dextran	0.005	0.054	0.5
NIPAAM	<0	<0	1.0
HPC	0.000	0.040	0.5

Within the marginal solvent regime, the mean distance between polymer chains is given by,

$$\xi \sim \frac{C^{\frac{3}{2}}a}{(1-2\chi)}\phi^{-\frac{1}{2}} \tag{5}$$

The volume fraction which defines the upper limit of marginal solvent behavior is given by Eq. (6), above which the polymer solution enters the theta regime.

$$\phi^+ \cong 1-2\chi \tag{6}$$

Within the theta regime, binary monomer–monomer contacts are eventually dominated by ternary interactions. Under these conditions, ξ is expressed as,

$$\xi \sim aC^2\phi^{-1}. \tag{7}$$

It follows from Eqs. (3)–(7) that, in applying models based on scaling relationships, it is important to recognize in which solvent regime the solution resides.

For the data gleaned from the literature, the polymer volume fraction concentrations which define the crossover points of solvent behavior were calculated using the physical properties listed in Table 2. The results are given in Table 4. For NIPAAM, whose interaction parameter is greater than 0.5, all concentrations in solution are considered to produce a theta solvent regime. It should be noted that the number of polymer systems considered for analysis were limited due to the existence, or non-existence, of values of the polymer physical properties necessary to determine concentration regimes.

2. Limitations of existing models

Hydrodynamic descriptions of solute transport within polymer solutions are based on the Stokes–Einstein equation for solute diffusivity. The solute is considered to move at a constant velocity in a continuum composed of the solvent, and this movement is resisted by frictional drag. Within the polymer solution, the polymer chains are considered to be centers of hydrodynamic resistance, fixed in place relative to the moving solute by entanglements and physical crosslinks. The polymer chains enhance the drag on the solute by slowing down the fluid near the polymer chain. A number of models have been derived based on this premise [1,2,10], which have been demonstrated to be effectively similar [11]. Therefore, the model of Cukier [2] will be used as representative of this approach. Cukier described the decrease in diffusivity as,

$$\frac{D}{D_0} = \exp(-k_C r_s \varphi^{\nu}) \tag{8}$$

in which k_C is an undefined constant for a given polymer–solvent system. The value of ν is determined by solvent–polymer interactions using the scaling descriptions provided before. While this model predicts the polymer concentration influence, its major limitation is that it does not account for the observed dependence of diffusivity on the solute radius.

Another model based on enhanced frictional drag is the hydrodynamic scaling model of Phillies [12]. This model is based on the ideas that the polymer chains in solution are not fixed but mobile, and that the dominant polymer–solute forces are hydrodynamic in nature. Once again, solute–polymer interactions are neglected. For small (<100,000 Da), solid solute probes, the model is expressed as,

$$\frac{D}{D_0} = \exp(-A r_s (M_p)^{0.5} \phi) \tag{9}$$

wherein A is a constant for a given polymer–solvent pair, and M_p is the polymer molecular weight. Again, the model has been demonstrated to provide a reasonable functional dependence on polymer solution concentration. However, as with the other hydrodynamic models, this equation does not capture the true dependence of diffusivity on solute size. Moreover, the model predicts that the molecular weight of the polymer in solution should influence solute diffusion, regardless of solute size. For large solutes (>250 Å) polymer molecular weight has indeed been found to influence solute diffusivity [13–15]. However, in studies of small (<200 Å) solutes, similar to those examined in this work, it has been demonstrated that polymer molecular weight has no significant impact on solute diffusivity [11,14–16].

Models based on an obstruction approach assume that the presence of impenetrable polymer chains causes an increase in the path length for diffusive transport. The polymer chains allow passage of a solute molecule only if it can pass between the polymer chains. This approach was taken by Ogston et al. [6] who assumed that solute diffusion in the polymer solution occurs by a succession of randomly directed unit steps. The polymer solution is assumed to exist as a random network of straight, long fibers of negligible width, and the solute is considered to be a hard sphere. The unit step is taken to be the root mean square average diameter of spherical spaces residing between the fiber networks. From these assumptions, they expressed the ratio of the diffusion coefficient in the polymer solution to that in water as,

$$\frac{D}{D_0} = \exp\left[-\frac{(r_s + r_f)}{r_f}\sqrt{\varphi}\right] \tag{10}$$

The limitations of this model are the fixed dependence of D on polymer volume fraction, which neglects different polymer–solvent conditions, and the incorrect description of the effect of solute radius.

Johansson et al. [7] developed an obstruction model based on the idea that the polymer solution can be viewed as being composed of a number of cylindrical cells. Each cylindrical cell consists of an infinite polymer rod centered in a cylinder of solvent of a given radius. The average diffusivity of the solute within this cell was found by solving Fick's first law. The global diffusivity of the solute is then calculated by summing up the number of cells having a given radius multiplied by the average diffusivity within that cell. The distribution of the cell radii was calculated using an expression for the distribution of spherical spaces within a random network of straight fibers [17]. Their expression for the reduction in solute diffusivity is,

$$\frac{D}{D_0} = \mathrm{e}^{-\alpha} + \alpha^2\,\mathrm{e}^{\alpha} E_1(2\alpha) \tag{11}$$

where

$$\alpha = \varphi\left(\frac{r_s + r_f}{r_f}\right)^2 \tag{12}$$

and E_1 is the exponential integral. The model produced a satisfactory agreement to simulation and experimental results for solute diffusion in both polymer solutions and polymer gels. Furthermore, the correct dependence on solute size is predicted. However, the model under predicts solute diffusivities for large solutes in high polymer volume fraction solutions (>0.01) [7].

Recently, another physical model of solute diffusion in polymer solutions has been put forth by Petit et al. [4]. In this approach, solute diffusion is envisioned to occur via jumps of length $\xi \sim \beta\phi^{-\nu}$ within the solution. In this respect, it is similar to the Eyring jump theory of solute diffusion in liquids [18]. These jumps occur with a frequency k, and β is predicted to be a constant for a given polymer in solution. The polymer contribution to solute transport retardation is considered to arise due to friction and this friction is given by $k\xi^2$. Their expression for solute diffusivity within a polymer solution is,

$$\frac{D}{D_0} = \left(1 + \frac{D_0}{k\beta^2}\phi^{2\nu}\right)^{-1} \tag{13}$$

According to this approach, the value of ν is determined by scaling theory. It has been found through curve fitting Eq. (13) to experimental data that $k\beta^2$ varies with solute radius, decreasing as solute radius increases [19]. Since β is a constant, k, or the jump length, must be varying. This analysis is reasonable, as larger molecules could experience fewer jumps. However, the lack of a description of how k varies with solute size limits the applicability of the model. Furthermore, the fitted values of ν do not correspond to the scaling predictions. For example, the values obtained for solute diffusion in poly(vinyl alcohol) ranged from 0.55 to 0.65 for a PVA concentration range of 0.027–0.38 g/ml [19]. At these concentrations, PVA is well within the marginal solvent regime and therefore ν should be approximately equal to 1.0. Finally, activated jump theories are controversial in the diffusion in liquids area [18].

3. Obstruction-scaling model

Recently, a model based on physical obstruction of the solute molecule by polymer chains has been proposed to predict intra-gel solute diffusion [20,21]. In this interpretation, solute transport occurs if an opening between the polymer chains large enough to permit its passage is produced through the random thermal movement of the polymer chains. Thus, solute diffusivity is dependent on the probability of an opening of this size occurring. This probability is expressed as,

$$D = D_0 \int_{r^*}^{\infty} g(r)\mathrm{d}r \tag{14}$$

in which $g(r)$ is the distribution of opening radii between polymer chains, and r^* is the critical radius required to allow solute passage. By picturing the polymer solution as a random network of negligibly thin, straight polymer fibers, the distribution of radii, r, of the spherical spaces between the polymer chains can be expressed as [17],

$$g(r) = \frac{\pi r}{2R^2} \exp\left(-\frac{\pi}{4}\left(\frac{r}{R}\right)^2\right) \tag{15}$$

where R is the mean radius of this distribution.

The average opening between polymer chains is considered to be $\xi/2$ where ξ is given by the scaling relationships described before. Using these equations, the obstruction-scaling model has the following general expression,

$$\frac{D}{D_0} = \exp\left[-\pi\left(\frac{r_s + r_f}{\xi + 2r_f}\right)^2\right] \tag{16}$$

in which r_s is the radius of the solute probe, r_f is the polymer chain radius, and ξ is the mean distance between polymer–polymer contacts. Thus, within the marginal solvent regime, the obstruction-scaling model is written,

$$\frac{D}{D_0} = \exp\left[-\pi\left(\frac{r_s + r_f}{\kappa\phi^{-\frac{1}{2}} + 2r_f}\right)^2\right] \tag{17}$$

where,

$$\kappa \sim C^{\frac{3}{2}} a(1 - 2\chi)^{-1} \tag{18}$$

and within the theta regime,

$$\frac{D}{D_0} = \exp\left[-\pi\left(\frac{r_s + r_f}{\kappa\phi^{-1} + 2r_f}\right)^2\right] \tag{19}$$

where,

$$\kappa \sim aC^2. \tag{20}$$

Eqs. (18) and (20) define the scaling constant for the polymer–solvent pair.

The obstruction-scaling model equations were fit to the gathered literature data using a Levenberg–Marquardt nonlinear regression algorithm incorporated into a computer graphing software package (KaleidaGraph™). The applicability of the model was determined by analysis of the sum of squares of the residuals (SSR), the correlation coefficient (R^2), and the physical consistency of the returned value of the fitted parameter. The confidence interval (±) of the returned value, at the 95% confidence limit, was calculated using the sum of squares of the residuals as an estimate of the variance in the data.

4. Applicability of the obstruction-scaling approach

Application of the obstruction-scaling model to the literature data illustrating the influence of polymer concentration on solute transport is displayed in Fig. 3a–c. The model was fit to the data by lumping all the polymer terms and the scaling constant into one term, κ, which was considered adjustable. ν was fixed at the scaling theory value for the specific polymer–solvent conditions (see Table 4). Various values were chosen as initial guesses for the regression procedure to verify the uniqueness of the obtained regression parameters. By visual inspection, it is clear that the model provides a good agreement with the data. This observation is confirmed by an examination of the regression results listed in Table 5. The sum of squares of the residuals is very low and the correlation coefficients are all above 0.90.

Attention should be drawn to the polymer–solvent scaling constant values. If the model is physically consistent, then the returned values of the scaling constant, κ, should be statistically equivalent for all solutes diffusing in a given polymer solution, assuming that no solute–polymer interactions occur. For cases where this assertion can be tested, κ values are indeed statistically equivalent, within the 95% confidence interval. For example, κ for the various solutes diffusing in PVA is consistently around 1.05 Å. The constant of proportionality implicit in Eqs. (18) and (20), can be calculated using the regression results given in Table 5. The results are 0.0065, 0.0040, and 0.0094 for NIPAAM, dextran, and PVA, respectively. It appears that the proportionality constant is polymer-dependent, at least as can be ascertained with this small data set.

The ability of the obstruction-scaling approach to account for solute size is shown in Fig. 4. The regression results are listed in Table 6. The model is consistent with the experimental data. Furthermore, the fitted κ value for PEGs diffusing in PVA solution is statistically equivalent to the value obtained for the smaller solutes in PVA solution

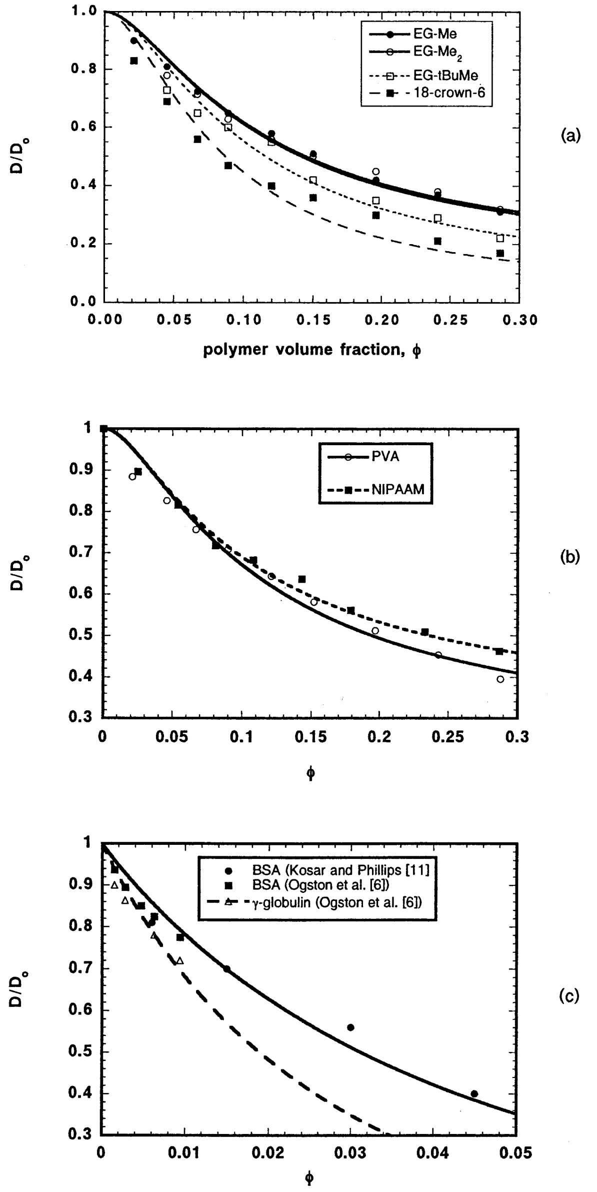

Fig. 3. Application of obstruction-scaling model to literature showing the effect of polymer volume fraction on solute diffusivity. Regression results are shown as lines and the regression results are given in Table 5. (a) Various solutes diffusing in PVA–water [19]; (b) self-diffusion of water in PVA and NIPAAM [16]; (c) BSA and γ-globulin in dextran–water solutions.

Table 5
Results of applying obstruction-scaling model to literature data of effect of polymer volume fraction

Polymer	Solute	ν	κ (Å)	±	SSR	R^2
PVA	EG-Me	1	1.04	0.03	0.005	0.985
	EG-Me$_2$	1	1.06	0.05	0.010	0.966
	EG-*t*BuMe	1	1.13	0.06	0.011	0.942
	18-crown-6	1	1.05	0.06	0.012	0.938
	Water	1	0.88	0.05	0.008	0.978
NIPAAM	Water	1	1.13	0.04	0.004	0.986
Dextran	BSA	0.5	13.8	0.40	0.009	0.962
	γ-Globulin	0.5	15.6	0.80	0.003	0.859

(Table 5). The model has thus been shown to be able to predict the influence of both solute radius and polymer volume fraction for the same water–polymer system.

The obstruction-scaling approach thus seems to be successful in describing solute diffusion in polymer solutions. Not only does the model account for the observed polymer volume fraction and solute radius behavior, but also describes the influence of polymer chain flexibility on solute diffusivity. For example, Fig. 3b shows the self-diffusion behavior of water in PVA and NIPAAM. The data shows that the less flexible NIPAAM ($C = 10.6$) provided the least resistance to water diffusion while the PVA ($C = 9$) provided the most. This behavior is captured in the scaling feature of the model which predicts that ξ will increase as C increases at a given polymer volume fraction (Eq. (5)).

The assumptions of the model require discussion at this point. The model relies on the depiction of a polymer solution, first proposed by Ogston [17], as a random network of straight fibers. Clearly, the polymers examined here cannot be considered rod-like, however, the assumption of randomness in the depiction allows the model to approach the distribution expected of more flexible chains and so this assumption can be considered reasonable. The model also assumes that the scaling theory proposed by Schaefer is correct. This theory is well supported by experimental evidence [22,23] and so the use of the theory seems valid. Further, the model tacitly assumes that the diffusion of solutes in water in the absence of polymer can be described by the Stokes–Einstein theory. No diffusion in liquids theory has been demonstrated to be completely predictive, however the Stokes–Einstein theory has been demonstrated to be reasonably effective [8]. Moreover, it has been demonstrated by Bu and Russo [14] and by Nyden et al. [24], that models based on the assumption that the solute is essentially a hard, hydrodynamically equivalent sphere cannot account for the greater than predicted diffusivities of high molecular weight flexible coil polymers in solutions of other polymers. Polymer coils exhibit non-draining behavior when their size is smaller than the correlation length of the matrix and they can therefore be treated as hydrodynamic spheres. Once the molecular weight increases beyond this restriction, models based on hard sphere solutes predict a greater restriction to diffusion than is observed experimentally because the polymer coil can modify its shape to pass through the available opening.

Table 6
Results of applying the obstruction-scaling model to literature data illustrating the influence of solute hydrodynamic radius

Polymer	Solute	κ	±	SSR	R^2
PVA	PEGs	1.17	0.04	0.007	0.871

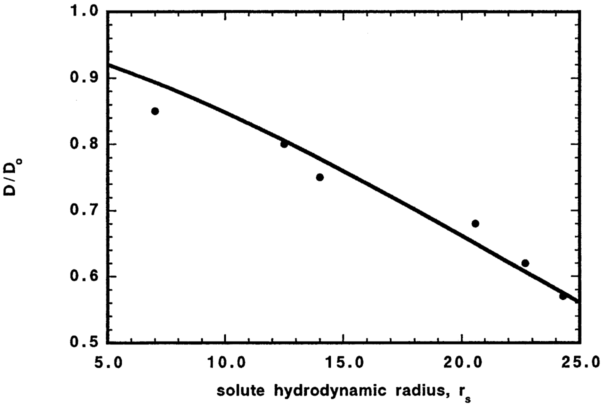

Fig. 4. Application of obstruction-scaling model to data illustrating effect of solute radius. The lines represent fits to the data and the regression results are given in Table 6.

Table 7
Regression results of fit of Eq. (17) to data of Bu and Russo of dextrans diffusing in HPC

FITC-dextran molecular weight (kDa)	r_h (Å)	κ (Å)	±	R^2	SSR
9	18.1	8.41	0.32	0.976	0.003
20	27.8	8.38	0.21	0.991	0.002
70	58	11.97	0.54	0.978	0.009
150	88.5	16.89	0.44	0.994	0.003
2000	179.0	21.88	0.33	0.999	0.001

To illustrate this point, the data of Bu and Russo [14], for FITC-dextrans of molecular weights ranging from 9 to 2000 kDa, is examined in more detail. The results of applying Eq. (17) to the data are listed in Table 7. From Table 7, one can see that, as r_h increases beyond 28 Å, κ increases, while for the two solutes below this limit, κ is constant at 8.4 Å. This result means that, in order for the model to fit the data appropriately, the average opening between polymer chains must increase as r_h increases beyond 28 Å. Clearly, this cannot be true. By considering the true value of κ to be 8.4 Å, theoretical curves were drawn to the data in Fig. 5. The figure demonstrates that the larger polymer solutes cannot be considered to be non-draining inflexible and spherical solutes. The higher than predicted D for these solutes must arise from another mechanism, possibly reptation.

Finally, the data set of experimental results has been taken from those polymers whose physical properties are well characterized. This data set is rather limited, which hampers the ability to discern the applicability of the model. A need exists for more experimental studies to determine diffusivities in other well defined polymer systems. More data could help either prove or disprove this model (and other models). Data are particularly needed in the area of the effect of solute probe radius on diffusivity.

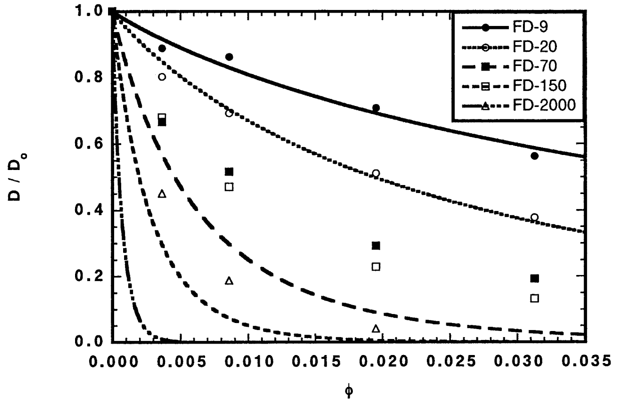

Fig. 5. Illustration of influence of polymer solute chain flexibility enhancing diffusivity above that predicted using a solid solute assumption. As polymer solute size increases, the predicted diffusivity is much lower than that observed experimentally.

5. Conclusions

An obstruction-scaling model has been presented and shown to successfully account for the influence of polymer volume fraction and solute size on a solute's diffusivity in aqueous polymer solutions for a variety of polymer systems. The model does not account for solute–polymer interactions, which have been found to be significant in certain cases [19,25]. Furthermore, the model is limited to predicting diffusivities of solutes which are essentially hard spheres in semi-dilute solution.

References

[1] Altenberger AR, Tirrell M, Dahler JS. J Chem Phys 1986;84(9):5122–30.
[2] Cukier RI. Macromolecules 1984;17:252–5.
[3] Phillies GDJ. J Phys Chem 1989;93(13):5029–39.
[4] Petit JM, Roux B, Zhu XX, Macdonald PM. Macromolecules 1996;29(18):6031–6.
[5] Mackie JS, Meares P. Proc R Soc Lond A 1955;232:498.
[6] Ogston AG, Preston BN, Wells JD. Proc R Soc Lond Ser A 1973;333:297–316.
[7] Johansson L, Elvingston C, Lofroth J-E. Macromolecules 1991;24:6024–9.
[8] Flynn GL, Yalkowsky SH, Roseman TJ. J Pharm Sci 1974;63(4):479–510.
[9] Schaefer DW. Polymer 1984;25:387–94.
[10] Phillips CG, Jansons KM. Macromolecules 1990;23:1717–24.
[11] Kosar TF, Phillips RJ. AIChE J 1995;41(3):701–11.
[12] Phillies GDJ. Macromolecules 1987;20:558–64.
[13] Turner DN, Hallet FR. Biochim Biophys Acta 1976;451:305–12.
[14] Bu Z, Russo PS. Macromolecules 1994;27(5):1187–94.
[15] Furukawa R, Arauz-Lara JL, Ware BR. Macromolecules 1991;24:599–605.
[16] Masaro L, Ousalem M, Baille WE, Lessard D, Zhu XX. Macromolecules 1999;32:4375–82.
[17] Ogston AG. Trans Faraday Soc 1958;54:1754–7.
[18] Tyrrell HJV, Harris KR. Diffusion in liquids. Toronto: Butterworths, 1984.

[19] Masaro L, Zhu XX. Macromolecules 1999;32:5383–90.
[20] Amsden B. Polym Gels Networks 1998;6:13–43.
[21] Amsden B. Macromolecules 1999;32(3):874–9.
[22] Hu Z, Li C, Li Y. J Chem Phys 1993;99(9):7108–14.
[23] Davidson NS, Richards RW, Maconnachie A. Macromolecules 1986;19:434–41.
[24] Nyden M, Soderman O, Karlstrom G. Macromolecules 1999; 32(1):127–35.
[25] Matsukawa S, Ando I. Macromolecules 1997;30:8310–3.
[26] Brandrup J, Immergut EH. Polymer handbook. New York: Wiley, 1999.
[27] Mark JE, editor. Polymer data handbook. Toronto: Oxford University Press, 1999.
[28] Zeng F, Tong Z, Sato T. Sci China Ser B Chem 1999;42(3):290–7.
[29] Marsano E, Gagliardi S, Ghioni F, Bianchi E. Polymer 2000;40:7691–8.
[30] Mays JW. Macromolecules 1988;21(11):3179–83.
[31] Petit JM, Zhu XX, Macdonald PM. Macromolecules 1996;29(1):70–76.
[32] Tokita M, Miyoshi T, Takegoshi K, Hikichi K. Phys Rev E 1996;53(2):1823–7.
[33] Johansson L, Skantze U, Lofroth J-E. Macromolecules 1991; 24:6019–23.
[34] Tyn MT, Gusek TW. Biotechnol Bioengng 1990;35:327–38.
[35] Zhu XX, Masaro L, Petit JM, Roux B, McDonald PM. Self Diffusion of Solvents and Solute Probes in Polymer Solutions and Gels: The Use of a New Physical Model of Diffusion. In: McCulloch I, Shalaby SW, editors. Tailored Polymeric Materials for Controlled Drug Delivery Systems. ACS, 1998.