Diffusion in Aqueous Solutions of Poly(ethylene glycol) at Low Concentrations

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ABSTRACT: We have observed the scaling behavior of the diffusion coefficient of poly(ethylene glycol) (PEG) ranging from dimer to n-mer of 14 000 ethylene glycol units in D_2O and in a (1:1) mixture of D_2O and diethylene glycol, solvents of both low and moderate viscosities. The accepted scaling relationship for diffusion of polymers at infinite dilution is $D_0 = KM^{-a}$, where a ranges from 0.5 for a Θ solvent to 0.6 for a good solvent, as originally proposed by Flory. Measuring D_0 as the extrapolated value of D versus concentration in a PGSE-NMR experiment, we find a surprisingly good fit to this scaling relationship over the entire molecular weight range for both solvent systems. The values of a obtained in D_2O at 25 °C, D_2O at 5 °C, and a D_2O/diethylene glycol mixture at 25 °C were 0.597 ± 0.020, 0.534 ± 0.021, and 0.542 ± 0.058, respectively. The extension of the scaling behavior down to the dimer species is believed to be due to the high local segmental friction coefficient of the ethylene oxide unit.

Introduction

The diffusion coefficient is of fundamental importance in polymer solution dynamics. The self-diffusion coefficient provides a measure of the rms translational motion of the polymer chains directly. The scaling of diffusion coefficients with polymer molecular weight in solution has received considerable attention.[1−19] Much of this work has focused on solutions in dilute and semidilute regions. One practical application of this scaling is its use in evaluating molecular weights of polymers based on measured self-diffusion coefficients. It was also observed that for polydisperse samples with continuous distributions, the self-diffusion coefficients in dilute solution scale with the weight average molecular weight (M_w) of the polymer.[20,21] At infinite dilution, Flory's scaling law[18,19] for polymer diffusion has been remarkably successful.

Linear poly(ethylene glycol) (PEG) is an unusual polymer in that it is soluble in a variety of different solvents with different functional groups. Possible aggregation of the polymer in solution makes determining its structure and dynamics of additional interest. A considerable amount of data is available on diffusion of PEG. This work includes studies of the mutual-diffusion coefficient,[9−11] self-diffusion coefficient,[12,13] or both.[14−16] Much of the prior work has focused on the scaling behavior at infinite dilution, as a function of concentration, and in bulk as related to reptation. This prior work suggests that the scaling exponent at infinite dilution is between 0.39 and 0.6.[9,11,12,14,16] In the present work, we have extended investigations of the scaling behavior of the diffusion of PEG at infinite dilution over a wide molecular weight range to explore the extent over which scaling behavior occurs. Of particular interest is the determination of the lower molecular weight limit to scaling behavior. These lower molecular weight species are not easily studied with light scattering (because of low scattering intensity) or photobleaching (because of the large label attached to a small molecule). We have also varied the chemical composition of the solvent and temperature to assess their effects on polymer diffusion.

Flory's scaling law, derived from the hydrodynamic dependence of the diffusion coefficient is

$$D_0 = KM^{-a} \tag{1}$$

where the scaling coefficient a ranges from $^1/_2$ for a Θ solvent to $^3/_5$ for a good solvent. At the Θ point the polymer chain dimensions should not be perturbed upon dissolution. At this point the rate of increase of the radius of gyration with increasing molecular weight is smallest. As the thermodynamic quality of the solvent increases, a polymer chain becomes more extended in solution. The more extended a polymer chain is in solution, the greater the increase in the radius of gyration with the addition of monomer units. Thus a goes from a minimum of $^1/_2$ (weaker molecular weight dependence) for a Θ solvent to a maximum of $^3/_5$ (stronger molecular weight dependence) for a very good solvent.[18] A branched polymer will have a maximum value of a less then $^3/_5$, since even in a very good solvent it cannot be as highly extended as a linear polymer. This small, but measurable, difference can be used to assess the molecular response to different solvent environments. For eq 1 to hold, K must be molecular weight independent. For this to be true at least one of two conditions must be met. The first condition is that the continuum limit has been reached, where the radius of gyration does not increase with the addition of one more monomer units to the chain. The second is that the asymptotic limit has been reached where the radius of gyration does not increase with increasing ζ/η_0, where ζ is the segmental friction coefficient of the solute and η_0 is the viscosity of the pure solvent.[18]

The constants in eq 1 are related to the constants in the Mark−Houwink−Sakurada equation[18]

$$[\eta] = K'M^{a'} \tag{2}$$

by the relationship

$$a' = 3\left(a - \frac{1}{2}\right) + \frac{1}{2} \tag{3}$$

so that a' will be correlated with a and range from $^1/_2$

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Table 1. Molecular Weight (g/mol) and Polydispersity for the PEG Samples

sample	$10^{-3}M_w$	$10^{-3}M_v$	PD	source
PEG-106	0.106		1.00	Aldrich
PEG-150	0.150		1.00	Aldrich
PEG-194	0.194		1.00	Aldrich
PEG-200	0.200			Aldrich
PEG-400	0.400			Fisher
PEG-2960	2.96		1.03	Aldrich
PEG-5660	5.66		1.05	Polysciences
PEG-15T	15.1		1.25	Aldrich
PEG-80T		80.6	1.64[a]	Aldrich
PEG-325T		325	4.04[a]	Aldrich
PEG-632T		632	4.71[a]	Aldrich

[a] Based on M_v/M_n.

for a Θ solvent to $^4/_5$ for a good solvent. The relation between K and K' is more intricate.

Experimental Section

Diffusion coefficients were determined using pulsed-gradient spin-echo nuclear magnetic resonance (PGSE-NMR).[22-24] In PGSE-NMR, a spin-echo experiment is performed with magnetic field gradient pulses added which label positions in the sample with specific precessional frequencies. If diffusion occurs during the experiment, incomplete refocusing of the spins results, reducing the observed signal intensity, A. The amount of the reduction is given by[22-24]

$$A = A_0 \exp(-2\tau/T_2) \exp(-\gamma^2 G^2 D\beta) \qquad (4)$$

where $\beta = \delta^2(\Delta - \delta/3)$ and γ is the magnetogyric ratio of the nucleus, τ is the time between the radio-frequency (RF) pulses, T_2 is the spin–spin relaxation time of the nuclei, G is the magnetic field gradient strength, D is the self-diffusion coefficient, δ is the width of the gradient pulse, and Δ is the time from the start of the first gradient pulse to the start of the second gradient pulse. It τ is held constant, a plot of ln A versus β gives a straight line with a slope proportional to D.[22-24] The diffusion coefficients of several species in a mixture can be determined from a single set of spectra simply by applying eq 4 to the resonances of the individual species. For the systems studied here, proton spectra were acquired; therefore PEG was the only intense source of signal for the PEG/D_2O system. For PEG in a mixture of D_2O and diethylene glycol, the PEG and diethylene glycol resonances overlap; therefore sufficiently large gradient pulses had to be used to ensure that all the diethylene glycol signal was dephased.

The diffusion experiments were performed on either a JEOL FX-100 or a Varian VXR-200 which we have modified to perform the diffusion experiment. The standard used to determine the gradient strength G, was a 1/1 molar mixture of D_2O/H_2O which has a diffusion coefficient at 25 °C of 2.029×10^{-9} m^2/s.[25] Gradient strengths were varied between 5 and 20 Gauss/cm. The temperature was controlled by passing thermally regulated air over the sealed sample tube at a rate of 10 L/min.

All materials were used as received. The D_2O (Aldrich) was 99.9% deuterated. A list of the various molecular weights of PEG used and the suppliers is given in Table 1. In Table 1, M_w is given as well as the polydispersities (PD) for the polymers for which they were known or determined by GPC. For the three highest molecular weight samples, reliable GPC results could not be obtained. However, M_n (via membrane osmometry) and viscosity average molecular weight, M_v, could be obtained (using an Ubbelohde viscometer) for these polymers; therefore M_v is given in Table 1 and used for these polymers in the scaling plots. The polydispersities reported for these samples are actually M_v/M_n. Since M_v is closest to M_w, using M_v for these polymers should not significantly affect the scaling behavior.

Results

Diffusion coefficients of PEG in D_2O at 5 °C and at 25 °C and in a 1/1 mixture (by weight) of diethylene glycol (DEG) and D_2O (actually 48% by weight D_2O) have been determined. The solvent systems have viscosities of 1.5, 0.89, and 7.70 mPa s, respectively. Thus, the quality of the solvent was varied both thermodynamically (by temperature) and chemically (by composition). The measured self-diffusion coefficients, D, were estimated from the slopes of log A vs β, with the precision estimated as ±1 standard deviation. The accuracy error of the measurements is significantly higher, but generally less than ±10%.

The diffusion coefficients of different molecular weight PEGs at several concentrations were extrapolated linearly to infinite dilution,[11] as shown in Figures 1–3. In the region of interest here, a linear extrapolation consistent with a virial analysis is appropriate,[11,26] with polymer concentrations held to a few percent.[4,5] The issue of the appropriate form of the extrapolation is somewhat complicated.[27] However, there was little difference between the extrapolations of D or $1/D$ with concentration, except at the highest molecular weights. Here the cause was an obvious one: for large polymers with high molecular weights where the D's are small and where noise was greater, the $1/D$ extrapolation exaggerates the errors and provides a less satisfactory estimate of D_0. The data for D_2O as the solvent (Figures 1 and 2) was divided into A and B plots because the diffusion coefficient data cover 2 orders of magnitude in D. The absolute values of the slopes of the extrapolations generally decrease with increasing molecular weight. Diffusion experiments on the low molecular weight polymers could not be performed in the mixed solvent due to the overlap of the PEG signals with diethylene glycol; however, the higher molecular weight species had sufficiently low diffusion rates that large β values could be chosen where no measurable signal was left from the diethylene glycol. The diffusion coefficient of diethylene glycol in the mixed solvent was used as the D_0 value for diethylene glycol. Trends in the extrapolated slopes for the DEG/D_2O system were found to be similar to those in the D_2O systems.

For the diffusion of diethylene glycol and triethylene glycol in water at 25 °C (Figure 1), decreasing diffusion coefficients occur with decreasing concentrations. These molecules are small enough, that at these concentrations, the diffusion coefficient is relatively independent of concentration. We have extrapolated these results linearly for consistency. Simple averaging of the D's for these concentrations yield D_0's which are within experimental error of the extrapolations. Similar questions do not exist for the mixed solvent system since the value of D_0 for diethylene glycol was measured directly.

The values of D for the extrapolations (of D vs C) to infinite dilution shown in Figures 1–3 are given in Table 2. The logarithms of the D_0 values plotted versus the logarithms of molecular weight are shown in Figure 4. Equation 1 indicates that this should yield a straight line with a slope of $-a$ where the scaling theory is valid. Figure 4 also shows the linear least squares fit used to determine the value of a. The error bars for the points in Figure 4 were determined from standard deviations of the intercepts of the extrapolations in Figures 1–3. The error estimates for a were determined from the standard deviations of the slopes in Figure 4. At 25 °C, a was 0.597 ± 0.020 for D_2O, indicative of a thermodynamically good solvent, while a was 0.534 ± 0.021 for D_2O at 5 °C, much closer to that expected for a Θ

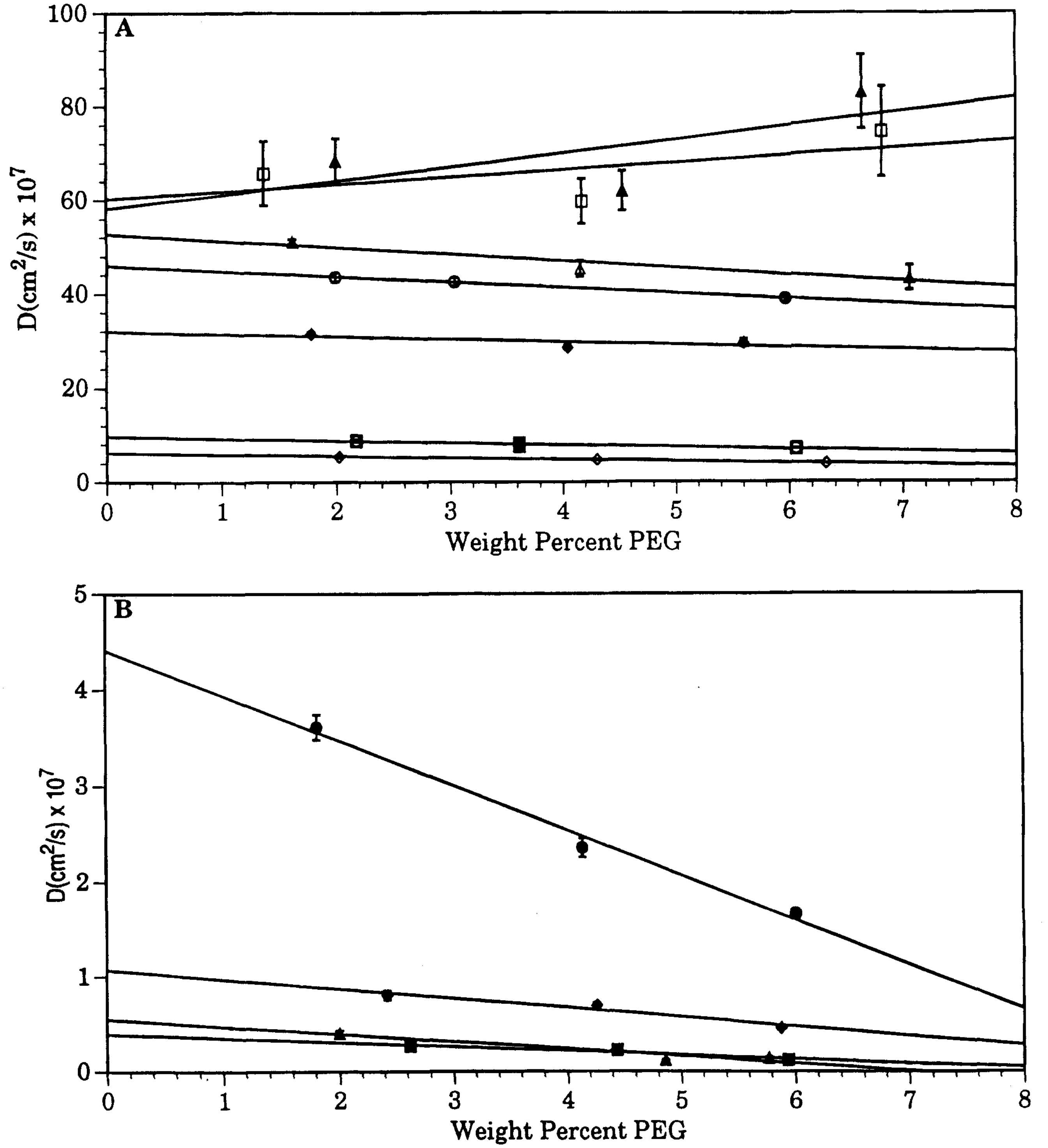

Figure 1. Self-diffusion coefficients of various molecular weights of PEG in D_2O at 25 °C as a function of concentration. (A) Lower molecular weight species: (□) 106, (▲) 150, (△) 194, (⊙) 200, (◆) 400, (⊡) 2960, and (◇) 5660. (B) Higher molecular weight species: (●) 15 100, (◆) 80 600, (■) 325 000, and (▲) 632 000.

solvent. The mixture of DEG/D_2O appears to be intermediate between the other two with an a of 0.542 ± 0.058. The larger error in this value makes this less conclusive.

Discussion

In all three solvent systems studied, scaling behavior is observed for D_0 as a function of molecular weight with a values consistent with theoretical expectations. From viscosity measurements on PEG in H_2O at 30 °C a value of $a' = 0.78$ was determined[28,29] which corresponds to $a = 0.593$ in the molecular mass range 20×10^3 to 5×10^6 g/mol. A scaling coefficient for PEG in water at 25 °C has also been determined over a smaller molecular weight range using dynamic light scattering by Brown and co-workers,[9,14] yielding a values of 0.58 and 0.61. These results are in excellent agreement with our data for D_2O at 25 °C ($a = 0.59_7$). In contrast, Kambe and Honda[11] reported a value of 0.391 for a at 25 °C, but did not offer an explanation for such a low value of a.

The value of a (0.53_4) at 5 °C indicated a thermodynamically *poorer* solvent quality at lower temperature. While this is the trend expected for most systems, especially nonpolar ones, it would appear to be incon-

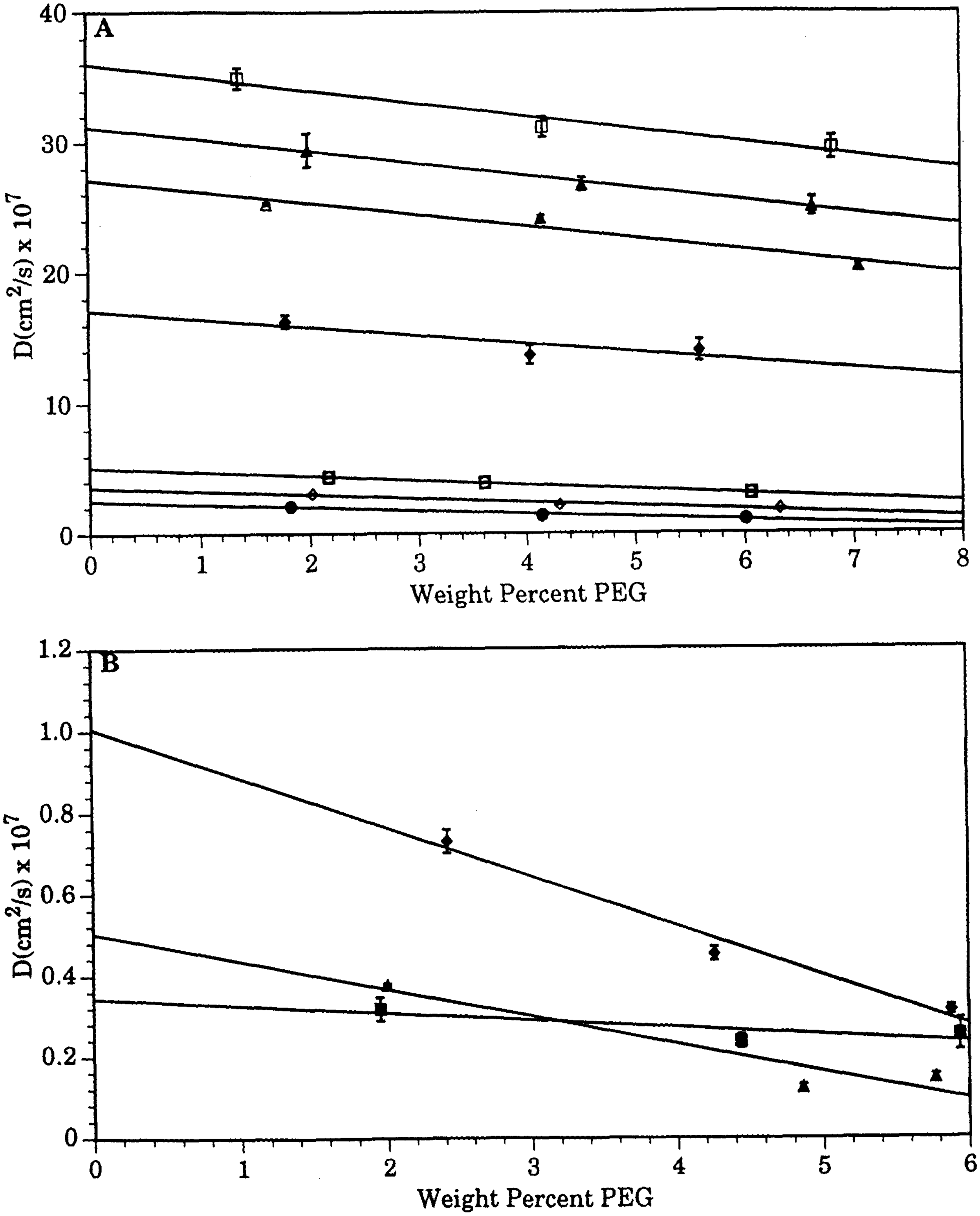

Figure 2. Self-diffusion coefficients of various molecular weights of PEG in D_2O at 5 °C as a function of concentration. (A) Lower molecular weight species: (□) 106, (▲) 150, (△) 194, (◆) 400, (⊡) 2960, (◇) 5660, and (●) 15 100. (B) Higher molecular weight species: (◆) 80 600, (■) 325 000, and (▲) 632 000.

Table 2. Self-Diffusion Coefficients for PEG Extrapolated to Infinite Dilution ($10^7 D_0$ (cm^2/s))

	molecular weight										
solvent	106	150	194	200	400	2960	5660	15.1k	80.6k	325k	632k
D_2O (25 °C)	60.3	58.2	52.8	46.0	32.0	9.71	6.23	4.41	1.07	0.397	0.551
D_2O (5 °C)	30.6	31.2	27.6		17.1	5.12	3.58	2.53	1.01	0.344	0.504
DEG/D_2O	19.2					2.12	2.06	0.914	0.220	0.138	0.284

sistent with thermodynamic data for the PEG/water system.[30] These data indicate that an immiscible region above about 100 °C is due to diminished hydrogen bonding; thus the solvent quality should become poorer

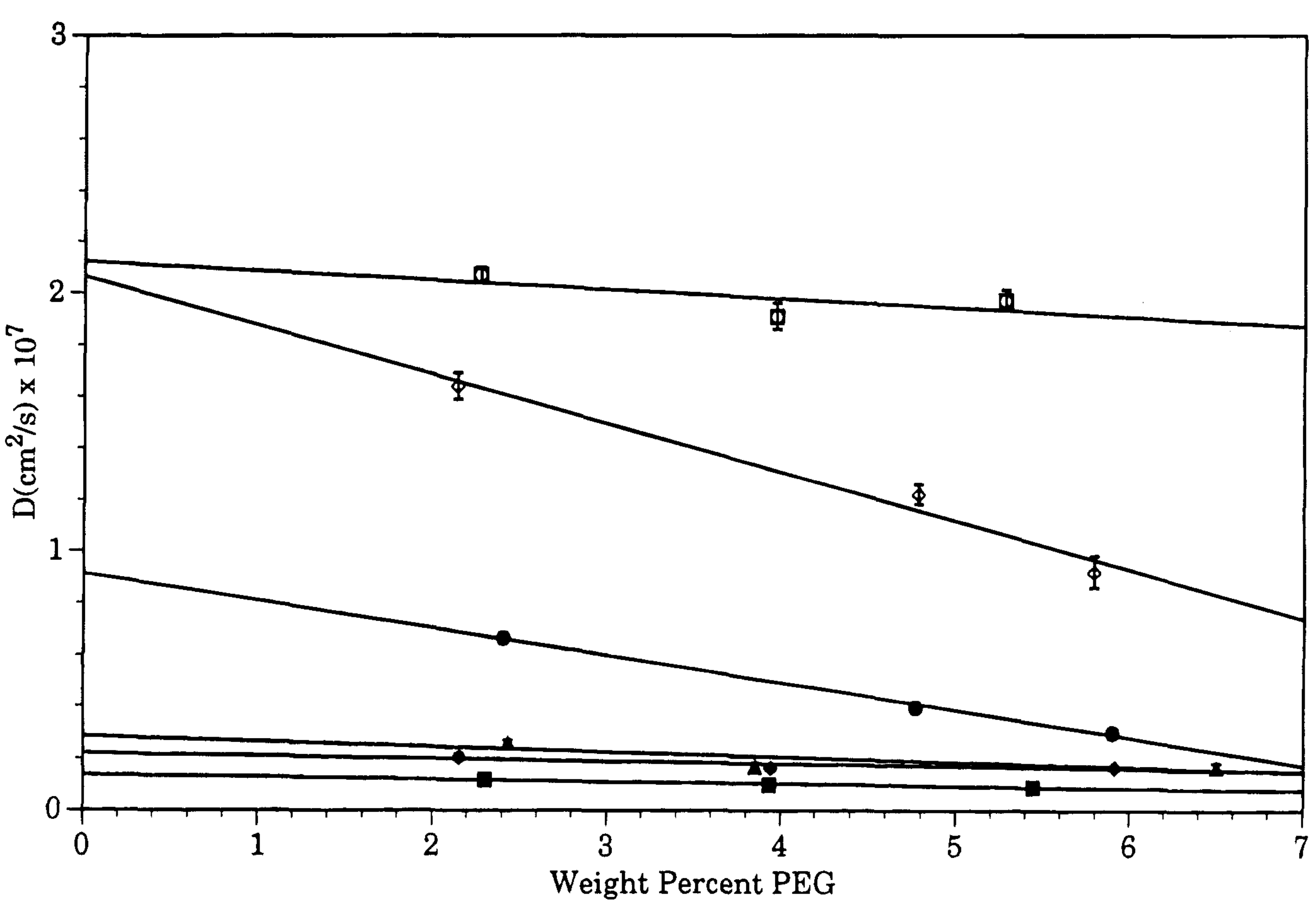

Figure 3. Self-diffusion coefficients of various molecular weights of PEG in a mixed solvent, 48 vt % D_2O and 52 wt % DEG, at 25 °C as a function of concentration: (⊡) 2960, (◇) 5660, (●) 15 100, (◆) 80 600, (■) 325 000, and (▲) 632 000.

Table 3. Scaling Behavior for PEG Solutions

source	basis	solvent	temp (°C)	α
this work	NMR	D_2O/DEG	25	0.542 ± 0.058
		D_2O	25	0.597 ± 0.020
		D_2O	5	0.534 ± 0.021
Bailey[30]	viscosity	H_2O	30	0.593
Tanner et al.[12]	NMR	H_2O	33	0.6
Brown et al.[9]	DLS	D_2O/H_2O	25	0.61
Brown[14]	NMR	D_2O/H_2O	25	0.58
Kambe et al.[11]	DLS	H_2O	25	0.391
Zhou et al.[16]	NMR	CH_3OH	25	0.5
Skirda et al.[8]	NMR	dioxane	60	0.51
		acetonitrile	60	0.57
		chloroform	60	0.54
		benzene	60	0.5
		dibutyl phthalate	100	0.57

with *increasing* temperature. Viscosity data indicate that water becomes a thermodynamically *better* solvent for PEG with increasing temperature up to about 45 °C.[31] This is consistent with what we have found here. The results for the mixed solvent also follow Flory's scaling law with a equal to 0.54, but the precision of this measurement was too low to allow an accurate determination of the thermodynamic quality of the solvent. Skirda et al.[8] have determined a for PEG in other solvents over a smaller molecular weight range and found that a varied between 0.5 and 0.57. These estimates were based on the molecular weight dependence of the chain overlap concentration, as indicated by the scaling of polymer diffusion coefficients as a function of concentration. Table 3 gives a summary of our results along with those from the literature.

In all three cases studied, the log D_0 data were fairly linear *over the entire molecular weight range.* It is not surprising that scaling behavior is found at high molecular weights. Diffusion studies on other systems[4-6,8,21] have not been extended below a molecular weight of a few thousand, except for the diffusion of poly(methyl methacrylate) (PMMA) in acetonitrile where the diffusion of an oligomer fell well below the scaling behavior for the polymer.[32] This is generally what we might expect for most polymer systems. We would not expect a dimer or trimer to follow this scaling law. However, the behavior of PEG in aqueous systems seems to be an exception.

As stated above, Flory cited two conditions, at least one of which must be met, in order for the scaling behavior to occur. The first is that the continuum limit has been reached where the radius of gyration does not increase with the addition of one more monomer to the polymer chain.[18] Obviously, this condition cannot be met by dimers and trimers. The second condition is that the asymptotic limit has been reached where the radius of gyration does not increase with an increase in ζ/η_0.[18] At constant η_0, ζ, the segmental friction coefficient of the solute, is sufficiently large that its increase would not change the end-to-end distance of the polymer chain. It is possible that this occurs because of a very high segmental friction coefficient for PEG in D_2O and in D_2O/DEG. Hydrogen bonding between the ether linkages of PEG and D_2O or the OH groups of DEG has been observed.[31] It has been reported that water binding to the PEG chains results in high chain extensions.[9] The high chain extensions of the oligomers and polymers

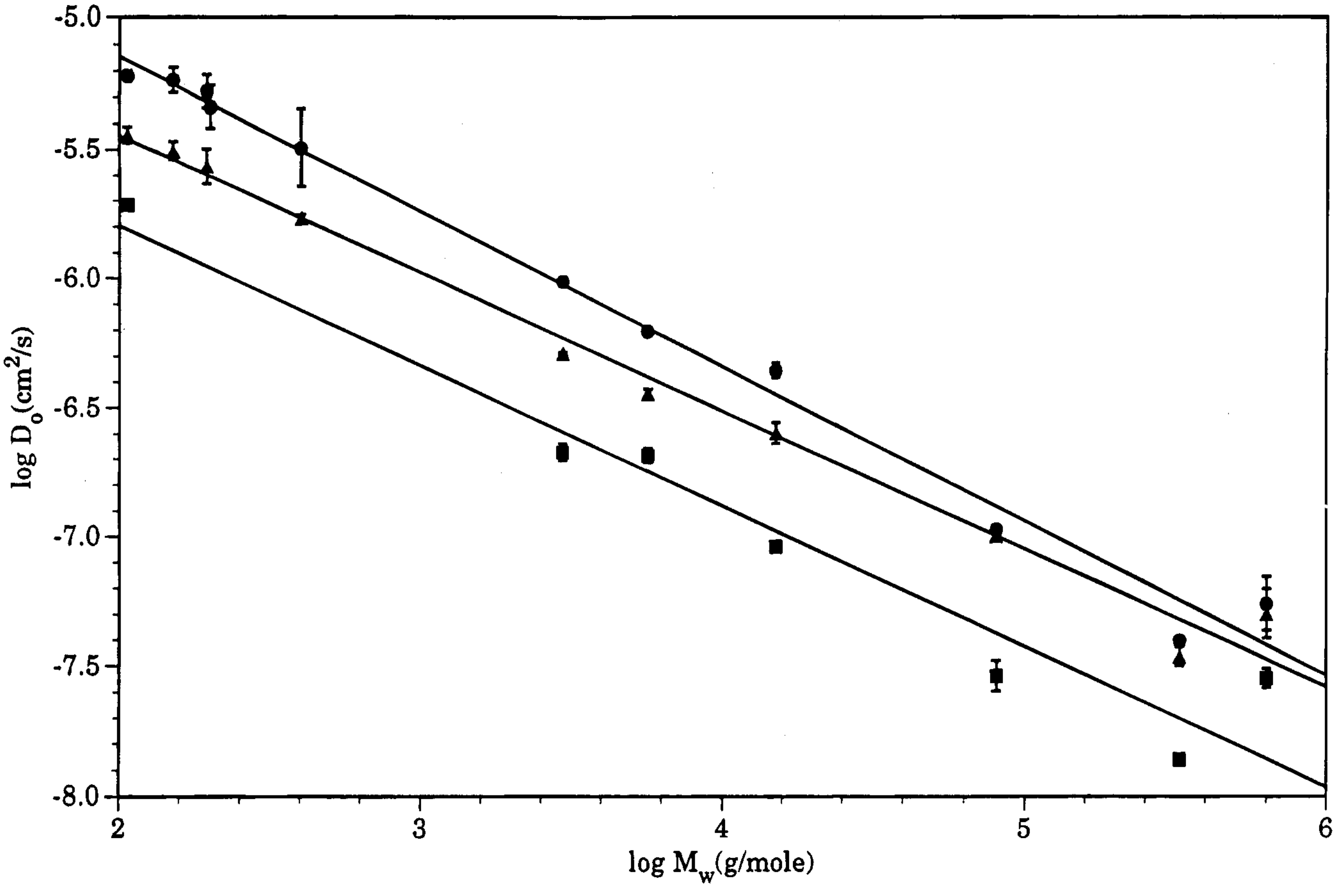

Figure 4. Plot of log D_0 versus log M_n for PEG in D_2O (●) at 25 °C and (▲) at 5 °C and (■) for 48 wt % D_2O/52 wt % DEG at 25 °C.

could then be responsible for the range of the scaling behavior observed.

Another possibility is that the observed behavior is fortuitous. Dynamic light scattering studies have shown evidence of aggregation in low molecular weight PEG solutions.[9,16,33] Apparently, only a very small fraction of PEG is found in aggregates and may be responsible for the "slow mode" diffusion observed with dynamic light scattering. The self-diffusion coefficients measured by PGSE correlate with the fast mode diffusion from dynamic light scattering, and both extrapolate to the same value at infinite dilution. Here aggregation should be limited,[16] especially for low molecular weight species, but if it occurred, it would lower the apparent diffusion coefficient. Countering this is the possibility that when eq 1 fails at low molecular weights, the slope steepens considerably, possibly to as much as −1.0.[34] This effect could restore the measured diffusion back into scaling behavior.

We prefer the former explanation that the broad range of scaling behavior observed here (down to monomer) is due to high chain extensions present in PEO in aqueous solutions. Nevertheless, since this is the first time this appears to be observed, other systems with high chain extensions should be studied for comparison.

Conclusions

PEG diffusion at infinite dilution follows Flory's scaling law in D_2O at 5 and 25 °C as well as in a mixed solvent of D_2O and DEG. These systems followed the predicted scaling behavior over the *entire* molecular weight range studied from diethylene glycol, with a molecular weight of 106, to a polymer with a molecular weight of 632 000. For a polymer to follow this scaling behavior all the way down to a dimer is unexpected, but hydrogen bonding between the solvent and polymer may give the polymer a sufficiently large segmental friction coefficient for this behavior to occur. We do not believe that this scaling behavior (down to monomer) is general, but believe it may occur in other systems with high local friction coefficients, possibly rigid polymers.

While our results agree with viscosity results,[31] i.e. water is a better solvent for PEG at 25 °C than at 5 °C, there is abundant evidence indicating that the immiscibility of PEG with water arises from diminished hydrogen bonding of solvent and polymer at higher temperatures.[30] As the temperature is increased, solvent quality should eventually decrease. Further measurements at higher temperatures, at closer proximity to the coexistence curve may help us to learn if this trend is indeed reversed when the immiscibility is approached.

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(27) The question of whether the more nearly linear result is obtained with a power series expansion of $D(c)$ or $(1/D)(c)$ is complicated both theoretically and experimentally. For example, Yamakawa's (and others) analysis relates D to the derivative of the osmotic pressure with respect to concentration, and there is no doubt that the analog in mixtures of the pressure in gaseous one-component systems can be represented by a virial expansion. Experimentally (for example: Wiltzius, P.; Haller, H. R.; Cannell, D. S. *Phys. Rev. Lett.* **1984**, *53*, 834 and references therein), it has been shown that the mutual diffusion coefficient—to which the self-diffusion coefficient reduces as a limiting value for dilute systems, and to which it is related by conservation—is more nearly linear than was expected from theory, extending several orders of magnitude in concentration. The rationale has been given both classically by Flory (*Principles of Polymer Chemistry*, p 306), where he states that the diffusion constant is the ratio of two functions each of which is a function of concentration, and by more recent theories (e.g., Ohta and Ohno. *Phys. Rev. Lett.* **1982**, *89A*, 460 and subsequent publications).
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