Probe Diffusion in Polymer Solutions under Θ and Good Conditions

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ABSTRACT: Quasielastic light scattering was used to measure the diffusion coefficient of 67-nm-diameter polystyrene latex spheres through aqueous solutions of $M_w = 1.39 \times 10^5$ (hydroxypropyl)cellulose at temperatures of 41 °C (near-Θ conditions) and 10 °C (good-solvent conditions). At both temperatures, D was described well by a stretched exponential form $\exp(-\alpha c^{\nu})$, with $\nu \approx 1$ under Θ conditions but $\nu \approx {}^3/_4$ in a good solvent. The observed solvent-quality dependence of ν is quantitatively predicted by several models of probe diffusion, including hydrodynamic scaling and the de Gennes-Langevin-Rondelez transient gel model.

Introduction

A good physical model of polymer dynamics in nondilute solution remains an object of research. Lodge et al.[1] concluded from their recent review of polymer solution and melt dynamics that "in entangled melts it (reptation) is often the dominant mode" but "it is unlikely that reptation is significant in the semidilute regime". Lodge et al. note a long series of different physical properties, including self-diffusion[2] and viscosity,[3] available to test particular models.

This paper treats probe diffusion, in which one observes the diffusion of mesoscopic particles through polymer solutions under different conditions, and seeks to infer the dynamics of polymer chains from the effect of the chains on the diffusion of the probes. Experimentally, probe measurements can be traced back to ultracentrifuge studies of Laurent and Pietruszkiewicz[4] and light scattering measurements by Turner and Hallett,[5] who measured the motion of proteins and of polystyrene spheres, respectively, through water/dextran. The use of probe diffusion measurements to test modern models of polymer solutions appears at least as early as the work of Langevin and Rondelez,[6] who made an extensive comparison between their own sedimentation data on probes in poly(ethylene oxide)/water and predictions based on transient statistical network models.

The diffusion of macroparticulate probes in water/(hydroxypropyl)cellulose (HPC), the topic considered here, has previously been studied by Brown and Rymden,[7,8] Yang and Jamieson,[9] and Russo and collaborators.[12,13] Their measurements, made at fixed temperature by means of light scattering spectroscopy, are consistent with a stretched-exponential relationship

$$D = D_0 \exp(-\alpha c^{\nu}) \qquad (1)$$

between probe diffusion coefficient D and HPC concentration c, α and ν being treated as adjustable parameters. Russo et al.[12] show the significance of bridging artifacts resulting from HPC adsorption by probe particles; they further demonstrate that small concentrations (0.01 wt %) of a surfactant (in their work, Triton X-100) are adequate to suppress bridging effects and cluster formation by the probe particles. There remains a disagreement in the literature[7,8,13] as to whether the Stokes-Einstein equation holds approximately in HPC solutions or whether semimacroscopic probe particles diffuse substantially faster through HPC solutions than would be expected from the macroscopic viscosity η of those solutions.

Unlike many of the other polymer/solvent combinations for which probe diffusion measurements have been reported, solvent quality in HPC/water depends strongly on temperature. On the basis of osmotic pressure, mutual diffusion, and sedimentation measurements, Bergman et al.[26,27] report that the HPC/water system has a lower critical solution temperature, with phase separation occurring at high T. At approximately 41 °C water is a near-Θ solvent for HPC; at lower temperatures, solvent quality improves, water at 25 °C being a good solvent for HPC. The exact nature of the Θ-like transition in HPC/water is a current topic of research.

Here we report a study of probe diffusion in HPC/H_2O far from and near to the Θ temperature. Through the temperature dependence of solvent quality, it is feasible to compare probe diffusion under near-Θ and good-solvent conditions, using the same polymer (indeed, the same samples) for both sets of measurements. The solvent quality has a strong effect on the concentration dependence of D, in a way consistent with some models of polymer dynamics but not others. The following sections of this paper give experimental procedures, our measurements of D, and a comparison with the literature.

Experimental Methods

The experimental techniques used in this work were virtually identical to those reported in our other recent papers,[15] so only a cursory summary is given here. The probe particles were 67-nm nominal diameter (Seradyn), carboxylate-modified polystyrene latex spheres. The solvent was deionized (14 MΩ) water to which 0.01 wt % Triton X-100 (Sigma) had been added to prevent polymer binding by the spheres; solutions were filtered through 0.2-μm microporous filters during addition of solutions to the sample cells. The matrix polymer was (hydroxypropyl)cellulose (Scientific Polymer Products, Ontario, New York, Catalog No. 401, Lot 1) of nominal molecular weight 60 000. Static light scattering intensity measurements find a weight-average molecular weight of 130 000 for this material.[10] Column chromatography followed by on-line multiangle laser light scattering and differential refractive index measurements obtain the complete molecular weight distribution;[11] moments of the distribution include $M_n = 89\,000$ and $M_w = 138\,000$. For studies of molecular weight effects, materials having a range of molecular weights, and a range of molecular weight distributions, would clearly be necessary. Our interest here was in the effect of solvent quality on probe diffusion, solvent quality being (relative to, e.g., viscosity) relatively independent of the molecular weight distribution.

Light scattering spectra of sphere/polymer/solvent mixtures were found to be completely dominated by scattering from the

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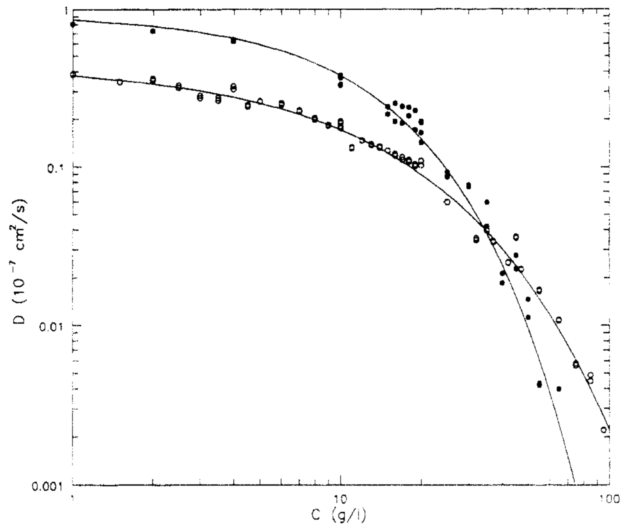

Figure 1. log–log plot of D of 67-nm polystyrene spheres in (hydroxypropyl)cellulose/H_2O/0.01 wt % Triton X-100 at 10 °C (open circles, good-solvent conditions) and 41 °C (filled circles, near-Θ conditions), as a function of polymer c. Solid lines are stretched exponentials (Table I, lines 1 and 3); note the absence of power-law (c^x) behavior.

probes, so D of the probes was inferred from the spectra of the mixtures without correction for polymer or solvent scattering. Control experiments using our probes in pure water gave good agreement with the expected Walden's rule ($D \sim T/\eta$) behavior over the full temperature range that we examined. To ascertain the effect of Triton X-100 on polymer binding by the probes, we performed titration experiments, measuring probe diffusion as a function of Triton X-100 concentration at fixed probe concentration. At 10 °C, below 0.01 vol % Triton X-100, D of the probes was in the range (2.2–2.8) × 10^{-9} cm^1/s; at and above the Triton X-100 concentrations that we employed, D suddenly doubled, to the range (4.8–5.4) × 10^{-9} cm^2/s. The transition is extremely sharp. Under Θ-like conditions (41 °C), the effect of Triton X-100 concentration on probe D is not substantial, D remaining constant to within 10% for Triton X-100 concentrations ranging from 1 × 10^{-5} to 0.1 vol %. However, at 41 °C the spectral variance V (the second cumulant from the scattering spectrum) is not substantially larger in our solutions than is V for the same probes in pure water, so there is little evidence for probe aggregation under near-Θ-like conditions.

Diffusion coefficient measurements were based on quasielastic light scattering, using primarily a He–Ne laser and 90° scattering angle. Temperatures were controlled by means of a computer-controlled circulating bath (Neslab) with a stability of 0.1 K. Spectra were obtained with a 144-channel digital autocorrelator (128 data channels, followed by a 1024-channel gap and 16 delay channels) and analyzed by the method of cumulants. Spectral signal-to-noise ratios (ratio of the $t = 0$ amplitude of the spectrum to the root-mean-square noise) were generally in the range 500–800. D of the probes was computed from the first cumulant obtained by the appropriately-truncated best-fit cumulant series. These solutions are not expected to have spatial correlations over distances $\lambda/(4\pi) \approx 500$ Å, so we did not make extensive measurements of the angular dependence of the spectrum. Our decision not to examine the angular dependence of the spectrum is supported by results of Russo et al.,[12] who had previously searched for a q-dependence of diffusivity in this system, in mixtures having larger polymer molecular weights; Russo et al.[12] did not find a substantial dependence of D on the scattering vector q.

Table I
Parameters and Fractional Root-Mean-Square Errors for Fits of Our Results to $D = D_0 \exp(-\alpha c^\nu)$ under Good and Near-Θ Solvent Conditions

solvent quality	T	D_0	α	ν	RMSE[b]
good	10	0.45	0.175	0.74	11
Θ	40.5	0.81	0.060	1.10	20.4
Θ	40.5	0.94	0.092	(1.00)[a]	21.2

[a] Parentheses denote a parameter held fixed rather than being adjusted. [b] RMSE: Root-mean-square fractional error, expressed as a percent.

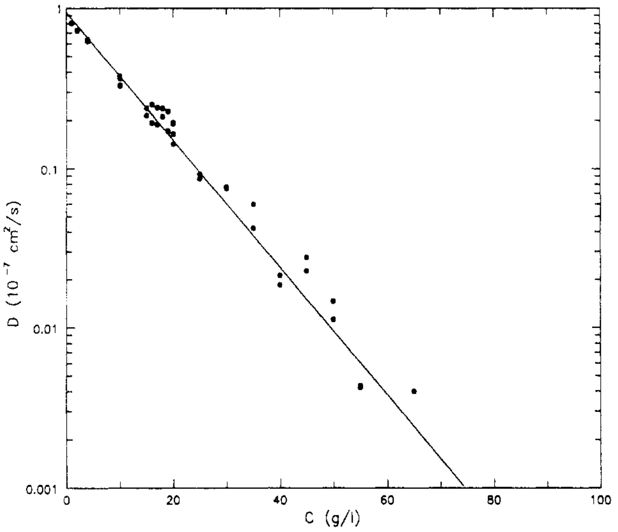

Figure 2. D of 67-nm polystyrene spheres in HPC solutions at 41 °C (near-Θ conditions). The solid line, using parameters from Table I, line 3, represents a simple exponential.

Results

Figure 1 presents our measurements of D of 67-nm polystyrene spheres in (hydroxypropyl)cellulose/water, given as a log–log plot of D against HPC concentration c. Filled circles represent data taken under near-Θ conditions (41 °C); open circles represent data obtained at 10 °C, remote from the Θ point. At both temperatures, D falls progressively with increasing c; at 60–100 g/L HPC, D is a 100-fold smaller than D in 0.1% Triton X-100/H_2O. Solid lines in Figure 1 represent nonlinear least-squares fits to eq 1. In this equation D_0, α, and ν were available to the nonlinear least-squares fitting program as free parameters. The curve displayed for the near-Θ condition data was obtained while imposing the constraint $\nu = 1$. Table I lists results of other fits.

From Figure 1, D is a smoothly-varying function of c. Within the scatter in the results, there is no indication of a linear region in either curve. Over a sufficiently narrow concentration regime, one could draw a tangent to either dataset and claim that one was observing scaling (i.e., $D \sim c^{-x}$) behavior, but this tangent could be placed equally well anywhere along the length of either curve, with any of a wide variety of possible slopes. The data shown here tolerate tangents with $0 \leq x \leq 2.8$ in a good solvent and $0 \leq x \leq 4.3$ under near-Θ conditions. However, the widths of regions over which the data could be said to lie on a single straight line are clearly not wide. We see no unambiguous indication of scaling-type behavior in our data.

Figure 1 emphasized the lack of power-law (scaling) phenomena. Figures 2 and 3 replot Figure 1 in semilog form to emphasize different features of the same measurements, namely, possible exponential or stretched exponential behavior. Figure 2 shows D against c under near-Θ conditions (41 °C); the solid line gives a simple exponential ($\nu = 1$ forced) fit. With this data, if one removes the constraint on ν and uses ν as a free parameter, one obtains $\nu \approx 1.10$. However, removal of the constraint on ν improves the fractional root-mean-square error in the fit by less than 5%. Under near-Θ conditions our measure-

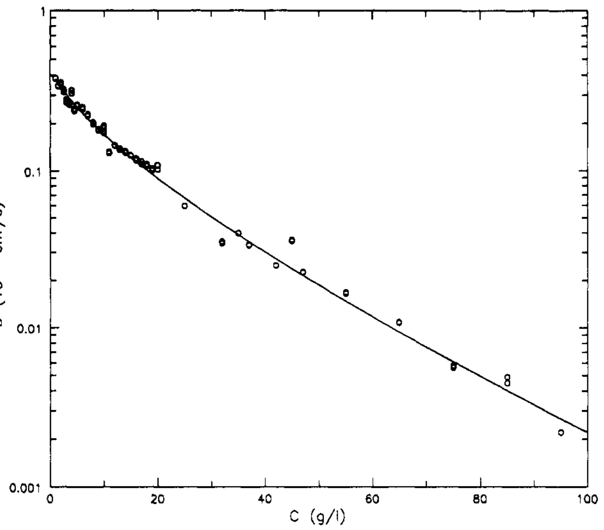

Figure 3. D of 67-nm polystyrene spheres in HPC solutions at 10 °C (good-solvent conditions). The solid line, using parameters from Table I, line 1, represents a stretched exponential.

ments are consistent with a simple exponential dependence of D on c.

Figure 3 shows D against c in relatively good-solvent conditions (10 °C). D is not described well as a function of c by a simple exponential. While one could put a single straight line near many of the data points, the plot of log D against c manifestly finds a smooth curve, not a straight line. The solid line in Figure 3 is a best-fit stretched exponential with $\nu \approx {}^3/_4$ (cf. Table I); the line clearly remains close to the measurements for $1.0 \le c \le 95$ g/L.

Discussion

This laboratory has previously reported the temperature dependence of D for polystyrene latex probes in nonneutralized poly(acrylic acid) (PAA)/water,[14] 2/3 neutralized poly(acrylic acid)/water,[15,16] and water/dextran.[17] Water is a good solvent for these polymers at all temperatures (typically 5–60 °C) that we examined. In the solutions studied previously, the temperature dependence of D was very nearly accounted for by the temperature dependence of the solvent viscosity coupled to Walden's rule; to first approximation $D \sim T/\eta$ in all polymer systems that we studied. In dextran solutions (but not in PAA solutions) D consistently increases with T very slightly faster than T/η, especially at large c (up to 300 g/L). The extent of the deviations from Walden's rule in water/dextran is virtually independent of polymer M. Since D_0 and D both scale with T as T/η, in all systems heretofore examined D/D_0 was nearly independent of T; the concentration dependence of D/D_0 in these systems was therefore also nearly independent of T.

In contrast to solutions of the above-mentioned polymers, in water/(hydroxypropyl)cellulose the functional form of the concentration dependence of D varies markedly with temperature. At 41 °C, D has a simple exponential relationship with c, but at 10 °C D varies with c in accord with a stretched exponential. This change in functional form is correlated with a change in solvent quality. The 41 °C data refer to near-Θ conditions, while the 10 °C data refer to good-solvent conditions. Equivalently, in terms of eq 1 ν depends on T, falling from 1 to 0.74 as T falls from 41 to 10 °C.

Our results on the response of probe diffusion to changes in solvent condition are consistent with the previous literature on HPC. Nystrom and Bergman[27] studied sedimentation of HPC at different temperatures. In dilute solution, the sedimentation coefficient s scaled as expected from η of the solvent. If one uses f and f_0 to denote the friction factors at elevated concentration and in the limit of infinite dilution, in concentrated solutions f_0/f falls with increasing c, the reduction in f_0/f being up to 2-fold more pronounced at 37 °C (near-Θ) than at 25 °C (good solvent). Nystrom and Bergstrom[27] thus found that the mobility f^{-1} decreases with increasing c, but more rapidly under near-Θ-solvent conditions than under good-solvent conditions. Similarly, at large c we find that the probe diffusion coefficient decreases more rapidly with increasing c under near-Θ-solvent conditions than under good-solvent conditions. A concentrated solution of polymers near the Θ point thus is more effective at retarding diffusion or sedimentation than is the same solution of the same polymer under good-solvent conditions. It should be recognized that (hydroxypropyl)cellulose/water is a relatively complicated chemical system, whose properties may be significantly sensitive to the presence of small amounts of surfactant (in our case, Triton X-100). We did not explore the extent to which our detailed quantitative results can be generalized to other surfactant concentrations, except that we did show that our probes aggregate significantly if the surfactant concentration is reduced.

How do our experimental observations compare with model-based concepts? We identify three groups of models that make predictions tested by the new results, namely, the reptation-scaling treatment of Langevin and Rondelez,[6] the hydrodynamic screening models of Altenberger et al.[21] and Cukier,[22] and the hydrodynamic scaling model.[19] We first summarize predictions and then compare with experiment.

Langevin and Rondelez[6] treat explicitly probe sedimentation, not probe diffusion, writing

$$s/s_0 \sim \exp(-(R/\xi)^\delta) \qquad (2)$$

with s the sedimentation coefficient, s_0 the low-concentration limit of s, R the probe radius, and ξ the coherence length, with $\xi \sim c^{-3/4}$ for neutral polymers. Equation 2 may be rewritten as

$$s/s_0 \sim \exp(-\alpha c^\nu) \qquad (3)$$

with $\alpha \sim R^1$. Because ξ is independent of M, ref 6 and eq 3 make the strong prediction $\alpha \sim M^0$. As shown by de Gennes,[20] the concentration dependence of ξ depends on solvent quality; de Gennes' models[20] predict $\xi \sim c^{-3/4}$ in good solvents (the result given in ref 6, but $\xi \sim c^{-1}$ near the Θ point. From eqs 2 and 3 one expects ν to be 0.75 or 1.0 under good or near-Θ conditions, respectively, so long as M is large enough for chains to entangle. Langevin and Rondelez's experiments found $\nu \approx 0.62 \pm 0.10$.

Altenberger et al.[21] consider hydrodynamic interactions between a particle and a porous gel, approximating the gel as a set of nonoverlapping blobs each of which acts as a point source of friction. If blob–solvent interactions are relatively weak, Altenberger et al. obtained an approximation for the friction factor of a spherical probe of radius R, which may be written as

$$D = D_0 \exp(-Q(c)) \qquad (4)$$

in which $Q(c) \sim c^\nu R^0$ for $\nu = 0.5$. While the dependence is not analyzed explicitly, in Altenberger et al.'s[21] model $Q(c)$ is determined by the blob–blob distribution function $g(c)$. Because $g(r)$ is nearly independent of M in the semidilute region, the Altenberger–Tirrell–Dahler treatment appears to imply that $Q(c)$, and hence the fractional retardation D/D_0 of diffusion by a polymer gel, should be nearly independent of M in the semidilute regime.

Cukier[22] treats the motion of a particle through a semidilute polymer solution via an effective medium description, making the key approximation that the polymer coils are fixed on the time scale of the particle motion. This approximation leads to the result that hydrodynamic interactions between the probe and the coil elements are screened, gaining a distance dependence $r^{-1} \exp(-\kappa r)$. Here κ^{-1} is an effective screening distance analogous to the Debye–Hückel screening length. Cukier's model gives $\kappa \sim c^{\mu}$ for $\mu = 0.5$; Cukier notes Freed and Edwards' prediction[23] $\mu = 1$ for an ideal chain and de Gennes' prediction[24] $\mu = 0.75$ for a swollen (good-solvent) chain. Evaluation of D of a probe within the Cukier model gives eq 1 or a linearized form $D = D_0(1 - \kappa R)$, with κ containing implicitly the concentration dependence of D.

The hydrodynamic scaling model[19] of polymer solutions relates the scaling exponent ν of eq 1 to the effects of coil contraction at elevated chain concentrations, via the model prediction $\alpha \sim R_g^3$. Following Daoud et al.,[18] one writes for the radius of gyration

$$R_g^2 \sim M^{\gamma} c^{-x} \tag{5}$$

Here γ depends on solvent quality; $\gamma \approx 1.2$ in a good solvent, but $\gamma \approx 1$ in a Θ solvent. Furthermore, $x \approx 1/4$ for large chains in good solvents, but $x \rightarrow 0$ for short chains, for any chain in the limit $c \rightarrow 0$, and for large chains in Θ solvents. From hydrodynamic scaling[19] ν is determined by x via

$$\nu = 1 - 2x \tag{6}$$

for self-diffusing chains, but $\nu \approx 1 - 1.5x$ for sphere probes. Combining the above results, $\nu = 1$ is predicted for near-Θ conditions, but $\nu < 1$ under good-solvent conditions. The limit $\nu = {}^5/_8$ is predicted to be attained for sufficiently large M; from an analysis of the literature[25] "sufficiently large" is apparently $\gtrsim 1 \times 10^6$. R_g falls with declining solvent quality, so from hydrodynamic scaling one would expect α to be significantly smaller under Θ than under good conditions.

Figures 2 and 3 provide the first experimental test of predictions of the effect of solvent condition on probe diffusion. Under near-Θ conditions, D shows a simple exponential dependence on c; i.e., under near-Θ conditions ν is unity. On the other hand, with the same polymer under good-solvent conditions D shows a stretched exponential dependence on c, with $\nu \approx 0.74$; changing from near-Θ to good solvents reduces ν substantially. The experimental findings are consistent with the Langevin–Rondelez treatment,[6] with Cukier's formulation of hydrodynamic screening,[22] and with the hydrodynamic scaling model but do not appear to be consistent with the $\nu \approx 0.5$ prediction of the formulation of Altenberger et al.[21]

The observed change in α with temperature, from 0.175 at 10 °C to 0.060 at 41 °C, is consistent with the hydrodynamic scaling prediction that α declines as solvent quality decreases. In eq 1 the Langevin–Rondelez and Cukier treatments apparently predict $\alpha \sim M^0 R^1$, while many experimental results[19] on probe diffusion follow roughly $\alpha \sim M^{0.8} R^0$, so the dependence on α on M and R tends to support the hydrodynamic scaling model[19] over alternatives. However, most theoretical treatments have emphasized polymer self-diffusion rather than probe diffusion, so their treatments of α may be incomplete; we therefore do not claim that our data provide a definitive confirmation of one model or another.

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