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Temperature Dependence of Probe Diffusion in Solutions of Low-Molecular-Weight Polyelectrolytes†

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ABSTRACT: Optical probe diffusion measurements were made on aqueous solutions of 2/3-neutralized poly(acrylic acid), molecular weights 5 and 150 kDa, both in salt-free systems and in systems containing 0.1 M NaCl. The probe particles were 204-Å-radius carboxylate-modified polystyrene latex spheres. The temperature dependence of the probe diffusion coefficient D_p is entirely explained by the temperature dependence of the solvent viscosity, no correction for a distance from a hypothesized glass temperature T_g of the solution being needed. For these systems, the hypothesis that the concentration dependence of D_p (as described by the universal scaling law $D_p = D_{p0} \exp(-\alpha c^\nu)$) is due to the concentration dependence of T_g, rather than being due to hydrodynamic interactions between polymer chains, is clearly rejected by our measurements.

Introduction

Notwithstanding several decades of effort, the elucidation of the nature of polymer dynamics in nondilute solutions remains a major theme for experimental and theoretical study. Ingenious experiments and theoretical efforts by a multitude of scientists have not yet resulted in complete agreement as to which forces dominate polymer dynamics, or how those forces are to be incorporated into an adequate model of coillike macromolecules in solution.

One way to gain information on polymer motions is to observe how a background of dissolved polymer molecules affects the diffusion of dilute mesoscopic probe particles.[1–14] While probe diffusion exhibits a rich phenomenology, several generalizations are noteworthy. Most experiments find[15] that the diffusion coefficient D_p of probe particles in polymer solutions follows

$$D_p = D_{p0} \exp(-\alpha c^\nu) \qquad (1)$$

Here α and ν are a scaling prefactor and scaling exponent, c is the concentration of the matrix (background) polymer, and D_{p0} is the nominal $c \rightarrow 0$ limit of D_p. The probes are always dilute. Phenomenologically,[15] one has $\alpha \sim R^\delta M^\gamma$, R and M being probe radius and matrix polymer molecular weight, respectively, while δ is generally 0 ± 0.2 and $\gamma \approx 0.9 \pm 0.1$. It is not always emphasized that eq 1 compares a series of measurements, all of which were taken at the same temperature.

This paper reports an experimental study relevant to the interpretation of optical probe measurements in polymer solutions. At issue is a possible explanation of the observed concentration dependence of D_p at fixed T, in terms of a putative dependence of the glass temperature T_g on polymer concentration c. It may reasonably be argued that T_g of a solution depends strongly on c, so measurements of D_p taken at fixed T and different c have been taken at very different values of $T - T_g$. Polymer transport properties, presumably including D_p, are generally said to depend near-exponentially on $T - T_g$. The universal scaling law eq 1 may then be proposed to be a glass temperature effect, in which the stretched exponential dependence of D_p on c arises from coupling a near-exponential dependence of D_p on $T - T_g$, to a dependence of T_g on c.

If this interpretation of eq 1 as a glass temperature effect were correct, plots of D_p against c at fixed $T - T_g$ (such plots requiring a different T for each c) might look very different from plots of D_p against c at fixed T. Under this interpretation, eq 1 would be an accident of the concentration dependence of T_g, not a fundamental statement about polymer dynamics. The objective of the work reported here is to test the hypothesis that eq 1 arises from T_g properties.

Experimental Section

We studied the diffusion of carboxylate-modified polystyrene latex spheres (hydrodynamic radius 204 Å) in solutions of 2/3-neutralized poly(acrylic acid) (PAA) of nominal molecular weights 5 and 150 kDa. Extensive results on probe diffusion in these poly(acrylic acids) has previously been reported;[10] however, all earlier work was performed with samples maintained at 25 °C.

Probe diffusion was studied in pure water, in 0.1 M NaCl, in salt-free polymer solutions, and in polymer solutions containing 0.1 M NaCl. Concentrations of the initial polymer stock solutions were measured by titration against NaOH. Experimental samples were prepared by dilution of the stock to concentrations in the range 1–100 g/L for the 5-kDa PAA and 1–45 g/L for the 150-kDa PAA. While there is an upper limit to the PAA concentration and ionic strength at which polystyrene spheres remain in stable suspension, in this work it was confirmed from the constancy of D_p over periods of days that our probe species is stable in the solutions we studied.

The experimental instrumentation and data analysis methods used here represent a gradual evolution from our previous experiments. Samples were filtered (generally through 0.1- or 0.2-μm pore size polycarbonate membranes) into precleaned light scattering cells (either glass fluorimeter cells, four sides polished, or disposable plastic fluorimeter cells (Markson)). For the scattering experiments, the cells were held in a massive copper mount through which thermostated water was passed. The bath stability was better than 50 mK. Samples were illuminated by a 20-mW He–Ne laser. In most cases, scattering through 90° was studied. The scattered light was detected with an RCA 7265 photomultiplier tube (typical photocurrent rates were (1–3) × 10^5/s); detected signals were passed through a preamplifier–discriminator circuit into either a 64- or a 144-channel Langley-Ford digital autocorrelator. Spectral integration times were 5–10 min. Signal-to-noise ratios (defined as the ratio of the amplitude of the spectrum to the root-mean-square random spread in the data R, defined below) were generally in the range 250–500.

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Spectra were analyzed by the method of cumulants,[16] in which the spectrum $S(k,t)$ is fit to

$$\frac{1}{2}\ln\left(S(k,t) - B\right) = \sum_{l=0}^{N} \frac{K_l(-t)^l}{l!} \qquad (2)$$

Here the K_l are the cumulants, while N is the truncation order of the cumulant series. The base line B was determined by delay channels spaced well out (for the 144-channel correlator, 1024 correlator channel widths) from the signal channels. The theoretical base line $B = P^2/n$, calculated from the total photocurrent P and the total number n of sample times in a run, agreed with the measured base line to within the limits imposed by the experimental signal-to-noise ratio. So long as it is recalled that taking the logarithm of $S(k,t) - B$ alters the point-by-point ratio of the random noise to the signal, thereby modifying the appropriate statistical weights for different data points, with well-behaved data there is no fundamental difference between making a weighted linear-least-squares fit to eq 2 and making a weighted nonlinear-least-squares fit for the K_l in

$$S(k,t) - B = \left[\exp\left(\sum_{l=0}^{N} \frac{K_l(-t)^l}{l!}\right)\right]^2 \qquad (3)$$

We used eq 2 and linear-least-squares fits.

The first cumulant is converted to the mutual diffusion coefficient via

$$D_m = K_1/k^2 \qquad (4)$$

where

$$k = \frac{4\pi n}{\lambda}\sin\left(\frac{\theta}{2}\right) \qquad (5)$$

Here k is the magnitude of the scattering vector, n is the index of refraction of the solvent, λ is the laser wavelength in vacuo, and θ is the scattering angle. The second cumulant, which is usefully expressed as the percent variance

$$V = 100\frac{K_2^{1/2}}{K_1} \qquad (6)$$

is a measure of the degree of nonexponentiality of the spectrum. A single exponential has a nominal V of 0. The particular lattices used here rarely exhibit V under 20–25% even at low concentrations in pure water.

The cumulant method is applied by fitting a given data set to a series of cumulants expansions, the expansions differing in their truncation orders N. To determine the most appropriate value of N, for each expansion the root-mean-square error

$$R = \frac{1}{M - N}\sum_{i=1}^{M}(D_i - T_i)^2 \qquad (7)$$

and the quality

$$Q = \frac{1}{M - N}\sum_{i=1}^{M-1}(D_i - T_i)(D_{i+1} - T_{i+1}) \qquad (8)$$

were evaluated. Here D_i is the measured content of correlator channel i, T_i is the value calculated for channel i from the cumulant expansion of order N, and M is the total number of correlator channels. The range of utility of the cumulant expansion, in terms of limits on acceptable signal-to-noise ratios and variances, has been explored by extensive (150 000 simulated spectra) Monte Carlo simulations.[17]

R and Q are merit parameters, indicative of the validity of a particular cumulant fit. With increasing N, both Q and R generally decrease. R has an intrinsic lower limit determined by the signal-to-noise ratio of the spectrum. Q declines at large N toward zero, sometimes becoming negative. In the large-N (but $N \ll M$) limit, the magnitude of Q is determined by the noise of the data, but the sign of Q is equally likely to be positive or negative. If, above some N, Q and R cease to improve as the fitting order is increased, N is the best fit—the highest order fit that can be supported by $S(k,t)$.

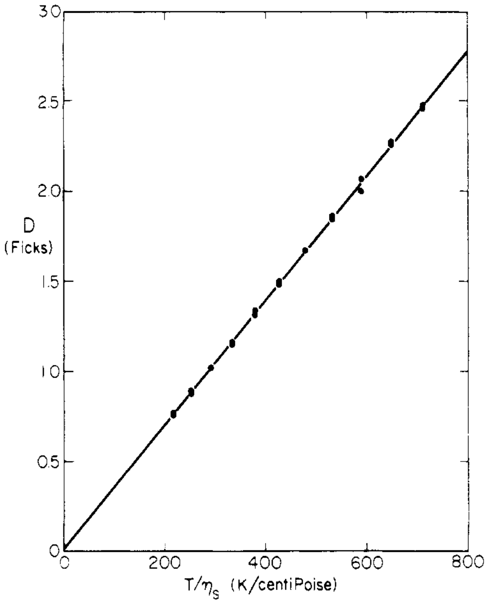

Figure 1. Diffusion coefficient of 204-Å-radius carboxylate-modified polystyrene spheres in pure water plotted against T/η_s, η_s being the solvent viscosity. Straight line indicates a linear-least-squares fit to eq 10.

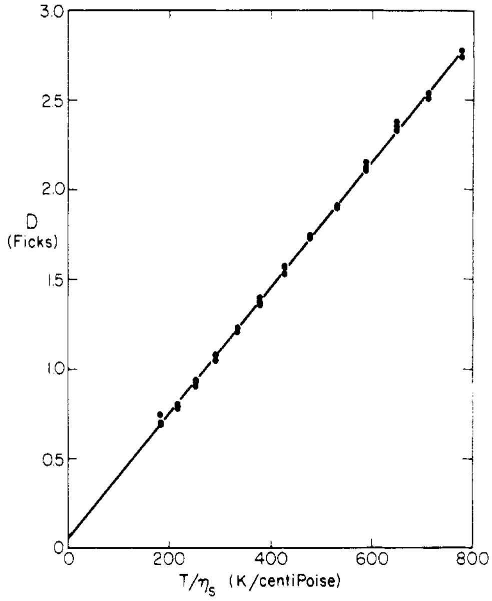

Figure 2. Diffusion coefficient of 204-Å-radius carboxylate-modified polystyrene spheres in 0.1 M NaCl:H_2O. Other details are the same as in Figure 1.

If one routinely calculates cumulants and merit parameters for a systematic set of truncated cumulant series (we always generated at least the first- through fourth-order cumulant expansions, for which $N \in (1,4)$), it is soon apparent that choosing the preferred truncation order is a significant practical issue often not discussed at proper length. One often finds that the random noise is so arranged that R and Q both continue to improve (by becoming smaller in magnitude) indefinitely as N is increased, the gradual progressive improvement in R and Q continuing to occur with very high fitting orders. This behavior would not be evident if one only evaluated R and Q for a single value of N or if one had a computer automatically select a single preferred fitting order. (In the work reported here, spectra were fit for a complete series of values of N, a preferred spectrum being selected by human intervention.)

To choose N, criteria beyond $\mathrm{d}R/\mathrm{d}N \cong \mathrm{d}|Q|/\mathrm{d}N \cong 0$ at the optimum N are clearly required. Four criteria beyond optimization of R and Q were imposed. First, $Q < 0$ is a clear indication that data points are randomly distributed around the fitting curve;

once $Q < 0$, a further increase in the fitting order is not justifiable. Second, N should be the same for similar spectra. One might observe that a series of samples having different c would require different values of N for a best fit, but multiple spectra of a single sample should be described successfully with a single value of N. Third, improvements in R and Q with increasing N are much more rapid when N is too small than when N is too large; clear breaks in $\mathrm{d}R/\mathrm{d}N$ and $\mathrm{d}Q/\mathrm{d}N$ occur near the optimal value of N. Finally, extensive Monte Carlo simulations of noisy spectra[17] make clear that there is an upper limit to the observed variance $V = 100K_2^{1/2}/K_1$, beyond which truncation of the cumulant series leads to unacceptable systematic errors in K_1. The computationally determined limit ($V \leq 65\%$ for the present correlator and signal-to-noise ratios) was respected throughout the work.

Computer control of the water circulator (Neslab, Inc.) and digital autocorrelator (LFI) permitted a full temperature series (generally 15–55 °C, sometimes 2–65 °C) to be run on a given sample without human intervention. Each sample was studied at multiple temperatures (typical ΔT between measurements was 5 K); at each temperature, three spectra were obtained.

Viscosities of the 150-kDa PAA in 0.1 M NaCl:H$_2$O were determined over a full range of temperatures by means of calibrated Cannon–Fenske and Ubbelohde viscometers placed in a stirred temperature-controlled bath. The viscosity η_s of pure water was taken from standard tables.[18]

Results

The bulk of our measurements appear the Supplementary Material (Tables and Figures 0–49, q.v.) as lists of temperatures and diffusion coefficients, followed by plots of D_p against T/η_s. This section summarizes those findings and correlates measurements of D_p, η, and η_s.

Polystyrene latex spheres are a traditional size standard, often used to ensure proper operation of nominally aligned QELSS systems. While the temperature dependence of D_p of spheres in pure water was at one time an object of controversy,[19] detailed measurements confirm that D_p of polystyrene spheres in water follows closely the solvent viscosity.[20]

If one writes

$$D_p = \left(\frac{k_B}{6\pi R}\right)\left(\frac{T}{\eta_s}\right) + b \tag{9}$$

where k_B is Boltzmann's constant, T is the absolute temperature, and R is the hydrodynamic radius of the probe, real data on D_p of polystyrene latex may be fit to eq 9 by treating R and b as fitting parameters. From this procedure one finds that R is quite close to the radius measured by electron microscopy, while b is within experimental error of 0. That is, the temperature dependence of the diffusion of polystyrene spheres in water, glycerol:water,[21] and sorbitol:water[21] is described well by Walden's rule, $D_p \sim T/\eta_s$.

For example, Fernandez et al.[20] measured D_p of polystyrene spheres in pure water for $T/\eta_s \in 200–600$ K/cP, so that $0.5 \leq D_p \leq 2.0$ (D_p reported in ficks: 1 fick = 1×10^{-7} cm^2/s). D_p measurements had an estimated error range of ±2%. Fernandez et al. found $R = 204$ Å (the nominal sphere radius, based primarily on electron microscopy, was 190 Å) and $b = -0.022$, b being within experimental error of $b = 0$.

Figures 1 and 2 (and Tables 0–7 of the Supplementary Material) represent D_p for polystyrene latex in pure water and in 0.1 M NaCl. Over the indicated temperature ranges (10–60 and 5–65 °C, respectively), D_p is linear in T/η_s. If one writes

$$D_p = A_0 + A_1\frac{T}{\eta_s} \tag{10}$$

for these two samples one finds $(A_0, A_1) = (0.006, 0.00347)$ and $(0.030, 0.00339)$, respectively. In both cases, a straight line clearly describes the data well; the intercept is close to its expected value $A_0 = 0$.

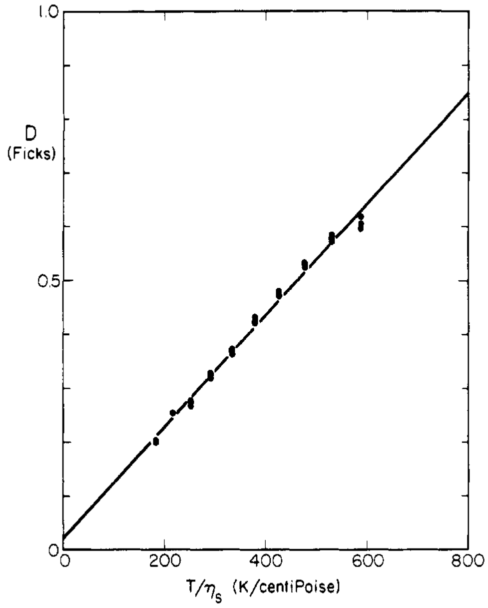

Figure 3. Diffusion coefficient of 204-Å-radius carboxylate-modified polystyrene spheres in 70 g/L of 5-kDa poly(acrylic acid), 2/3 neutralized, plotted against T/η_s, η_s being the solvent viscosity. Straight line indicates a linear-least-squares fit to eq 10.

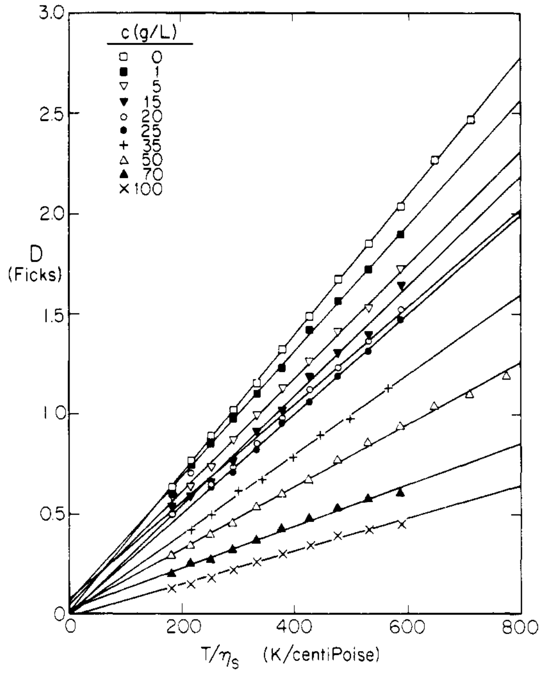

Figure 4. D_p against T/η_s for various PAA concentrations, elsewise the same as Figure 3. At each PAA concentration D_p shows Walden's law behavior.

Similar measurements were made on spheres in polymer and polymer:salt solutions. To ascertain the validity of eq 10, each temperature study was separately fit to eq 10 to a quadratic form

$$D_p = A_0 + A_1\frac{T}{\eta_s} + A_2\left(\frac{T}{\eta_s}\right)^2 \tag{11}$$

and to eqs 10 and 11 with A_0 forced to zero. The expected result is eq 10 with A_0 close to zero. A failure of Walden's rule might not be described well as a quadratic form. However, if there were a failure of Walden's rule behavior,

Table I
Linear Fit Parameters for D_p against T/η_s or (150-kDa PAA, 0.1 M NaCl) T/η

	5-kDa PAA 0 NaCl		5-kDa PAA 0.1 M NaCl		150-kDa PAA 0 NaCl		150-kDa PAA 0.1 M NaCl	
	c, g/L	linear	c, g/L	linear	c, g/L	linear	c, g/L	linear
A_0	1	5.62×10^{-2}	2	1.91×10^{-2}	1	5.40×10^{-2}	1	5.13×10^{-3}
A_1		3.13×10^{-3}		3.47×10^{-3}		3.95×10^{-3}		1.69×10^{-3}
χ^2		6.55×10^{-3}		1.33×10^{-3}		3.26×10^{-2}		1.17×10^{-2}
A_0	5	4.25×10^{-2}	5	4.63×10^{-2}	5	-6.99×10^{-3}	2	-7.84×10^{-3}
A_1		2.83×10^{-3}		3.34×10^{-3}		4.95×10^{-3}		1.19×10^{-3}
χ^2		3.03×10^{-2}		3.90×10^{-3}		6.15×10^{-3}		3.73×10^{-3}
A_0	15	-7.74×10^{-3}	25	5.80×10^{-2}	10	2.51×10^{-2}	5	-1.64×10^{-2}
A_1		2.73×10^{-3}		2.19×10^{-3}		5.84×10^{-3}		9.40×10^{-4}
χ^2		2.98×10^{-2}		1.21×10^{-2}		9.20×10^{-3}		4.65×10^{-3}
A_0	20	7.09×10^{-2}	50	-9.47×10^{-4}	15	5.41×10^{-3}	10	-4.15×10^{-3}
A_1		2.43×10^{-3}		1.36×10^{-3}		6.81×10^{-3}		7.92×10^{-4}
χ^2		5.34×10^{-2}		1.39×10^{-2}		7.17×10^{-4}		4.55×10^{-3}
A_0	25	-2.82×10^{-3}	75	1.94×10^{-2}	25	-1.05×10^{-2}	15	-9.99×10^{-3}
A_1		2.49×10^{-3}		9.42×10^{-4}		7.32×10^{-3}		7.30×10^{-4}
χ^2		2.38×10^{-3}		4.46×10^{-3}		8.29×10^{-4}		1.46×10^{-3}
A_0	35	-5.36×10^{-3}			35	1.40×10^{-2}	20	-3.93×10^{-3}
A_1		2.00×10^{-3}				7.10×10^{-3}		6.86×10^{-4}
χ^2		5.30×10^{-3}				7.12×10^{-4}		5.37×10^{-4}
A_0	50	1.00×10^{-2}			45	4.81×10^{-3}	25	-4.49×10^{-4}
A_1		1.56×10^{-3}				8.27×10^{-3}		3.98×10^{-4}
χ^2		9.67×10^{-3}				6.28×10^{-4}		3.70×10^{-4}
A_0	70	2.19×10^{-2}					30	1.49×10^{-3}
A_1		1.03×10^{-3}						3.28×10^{-4}
χ^2		4.938×10^{-3}						3.80×10^{-4}
a_0	100	-1.78×10^{-2}						
A_1		8.26×10^{-4}						
χ^2		2.94×10^{-3}						

a plot of D_p against T/η_s would reasonably be expected to deviate in intercept or curvature from simple straight-line behavior, so eq 11 is a reasonable test for failures of Walden's rule.

Figures 3 and 4, and Supplementary Material Tables 8–19, report probe diffusion in solutions of 2/3-neutralized (pH approximately 7) 5-kDa poly(acrylic acid) at concentrations of 1, 2, 5, 10, 15, 20, 25, 30, 35, 50, 70, and 100 g/L. These solutions contained no added background electrolyte, maximizing the opportunity for potentially interesting polyelectrolyte anomalies. Figure 4 shows measurements covering a range of polymer concentrations, while Figure 3 (ordinate expanded relative to Figure 4) confirms D_p is close to Walden's rule behavior at relatively large polymer concentration. The behavior of D_p is unremarkable, eq 10 with a minimal but generally nonzero intercept A_0 providing a good description of each set of measurements.

Table I presents coefficients obtained by fitting eq 10 to our measurements. For each solution, A_0, A_1, and χ^2 (the root-mean-square error) are reported. More elaborate or constrained fitting functions do not yield better descriptions of the data. As seen in Supplementary Material Table 20, replacing eq 10 with quadratic curves, or with a curve forced to pass through the origin ($D_p = 0$ at $T/\eta_s = 0$), generally has little effect on χ^2. Forcing $A_0 = 0$ in either equation increases χ^2, but in most cases by less than 10%. Except at the two highest polymer concentrations, there is no indication of any quadratic deviation from Walden's rule. At 70 and 100 g/L PAA, the two highest temperature points are significantly lower than expected from Walden's rule, a behavior described by introducing a small negative value for A_2; points at lower T/η_s fit well on a straight line.

The consequences of adding a small-ion electrolyte (here, 0.1 M NaCl) are indicated by Figure 5 and by Tables 21–28 of the Supplementary Material, which give D_p for 0.038-μm spheres at polymer concentrations of 1, 2, 5, 25, 50, and 75 g/L. The addition of NaCl slightly increases D_p at low polymer concentration, and perhaps slightly reduces D_p at higher concentrations, consistent with previous findings[10] that D_p is virtually independent of ionic strength in this system. At all polymer concentrations eq 10 gives a good description of D_p. Table 29 of the Supplementary Material provides fit parameters and χ^2 values for eqs 10 or 11 as applied to these measurements. For $c \leq 50$ g/L, D_p lies on straight lines which do not pass quite through the origin. Supplementary Material Table 29 shows that adding a quadratic fitting parameter has nearly no effect

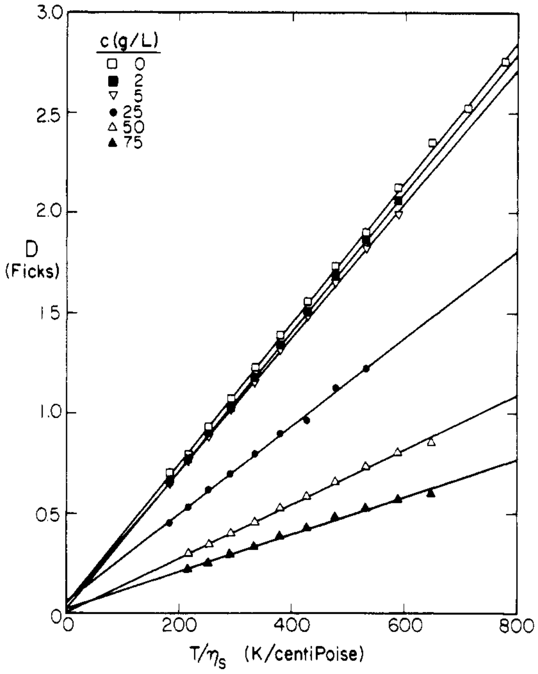

Figure 5. D_p of 204-Å-radius carboxylate-modified polystyrene spheres in 5-kDa poly(acrylic acid), 2/3 neutralized, at various concentrations, with 0.1 M NaCl, plotted as a function of T/η_s, η_s being the solvent viscosity. Straight lines are least-squares fits to eq 10.

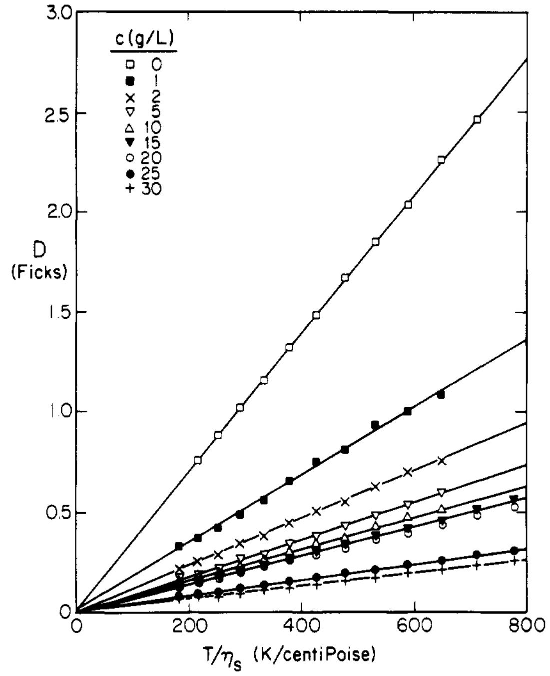

Figure 6. D_p of 204-Å-radius carboxylate-modified polystyrene spheres in 150-kDa poly(acrylic acid), 2/3 neutralized, at various concentrations, no added salt, plotted against T/η_s. Least-squares fits to eq 10 resulted in the straight lines.

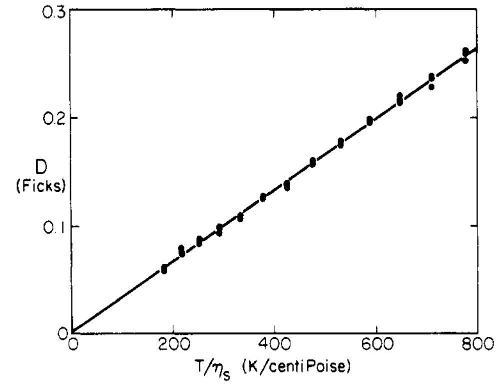

Figure 7. D_p against T/η_s for 30 g/L 150-kDa PAA. Data match Figure 6, with the ordinate expanded to clarify the behavior of a large-*c* sample.

on χ^2; linear fits forced to pass through the origin have significantly larger χ^2 than fits in which A_0 is a free parameter. Only at $c = 75$ g/L is there any indication of a quadratic correction term; ascribing to the data a small negative curvature ($A_2 = -1.6 \times 10^{-3}$) does improve the match between experiment and functional approximation, primarily at the highest two temperatures studied.

Diffusion by probes in solutions of 150-kDa poly(acrylic acid), 2/3 neutralized, no added simple electrolyte, is represented by Figures 6 and 7 and Supplementary Material Tables 30–40, which include polymer solutions with c = 1, 2, 5, 10, 15, 20, 25, and 30 g/L. Increasing the polymer molecular weight increases η and reduces D_p. At any polymer concentration, D_p is substantially smaller with the 150-kDa polymer than with the 5-kDa polymer. In each solution, Walden's rule is obeyed to good precision. Linear extrapolation of D_p to $T/\eta_s \rightarrow 0$ obtains intercepts that differ from $D_p = 0$ by little more than the scatter in the measurements.

Supplementary Material Table 41 contrasts different linear and quadratic models for measurements on 150-kDa PAA with no added salt. The simple linear fit gave parameters presented in Table I. Almost without exception, χ^2 values for linear and quadratic fits to a given temperature series, with or without intercept forced to zero, were nearly equal. Within the limits of experimental accuracy, the results support simple Walden's rule behavior in this system.

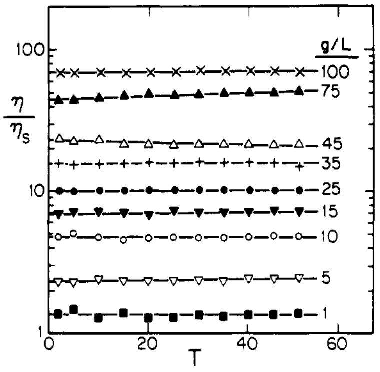

Figure 8. η/η_s as a function of temperature for solutions of 150-kDa PAA:0.1 M NaCl, showing that the temperature dependence of the solution viscosity η arises almost exclusively from the temperature dependence of the solvent viscosity η_s.

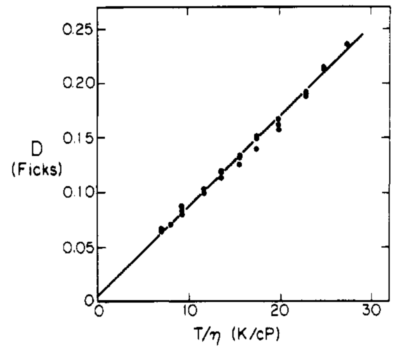

Figure 9. D_p against T/η for 204-Å polystyrene spheres in 45 g/L of 150-kDa PAA, 2/3 neutralized, 0.1 M NaCl, showing that D_p at fixed polymer c obeys Walden's rule.

Adding 0.1 M NaCl to 150-kDa PAA tends to increase D_p, the size of the effect being correlated positively with polymer concentration. Figure 8 shows the temperature dependence of the solution viscosity η of these systems, η/η_s being plotted against T. As apparent from Figure 8, η/η_s is independent of T; the dependence of η on temperature is governed entirely by the solvent viscosity.

Figure 9 shows D_p in 45 g/L 150-kDa PAA:0.1 M NaCl:H_2O. D_p is visibly linear in T/η; the D_p intercept is no larger than the scatter of the data points around the line. Complete measurements of D_p of spheres in 150-kDa PAA, 2/3 neutralized, with 0.1 M NaCl appear as Tables 42–48 of the Supplementary Material. Included are systems having polymer concentrations of 1, 5, 10, 15, 25, 35, and 45 g/L. In all these systems, eq 10 is a reasonable model for the data. Table 49 of the Supplementary Material shows fitting parameters for these data against eqs 10 and 11. The $T/\eta \rightarrow 0$ intercepts for fits to eq 10 are experimentally indistinguishable from zero, as witness the modest change in χ^2 attendant to forcing A_0 to be identically zero. In some cases, plots of D_p against T/η are better described by the quadratic equation (11) than by a linear equation. However, the improvements in the already small root-mean-square errors due to the use of quadratic models are small (<40%); furthermore, A_2 values from fits to eq 11 at a series of different polymer concentrations are not consistent as to sign or magnitude. We conclude that differences between linear and quadratic fits to D_p measurements are due to random chance, so the linear fits are to be preferred.

A fundamental question in the interpretation of QELSS spectra is the nature of the line shape. Simple models for QELSS spectra of probe:matrix polymer solutions implicitly assume that the relaxation modes of the system are exponentials, in which case the spectral variance V should be nearly zero. In pure water or 0.1 M NaCl, the probe spheres have spectral variances of 20–30%. Addition of either 5- or 150-kDa PAA systematically but modestly increases V. In 5-kDa PAA at either ionic strength, V is in the range 30–45%, while spectra are adequately described by a cumulant expansion truncated at $N = 2$ or 3. V becomes modestly larger in solutions of the 150-kDa polymer; with 0.1 M NaCl, V is 35–45%, increasing to 55–65% at 45 g/L PAA concentrations. In the absence of added salt, solutions of the 150-kDa PAA give V of 40–50%, little dependence on PAA concentration being apparent. Thus, with either polymer and either ionic strength, spectra are not far from exponential, while V is well within the range[17] in which the cumulant expansion (at our signal-to-noise ratio) gives reliable values for K_1 and D_p.

Discussion

Our principal experimental result is that the temperature dependence of D_p is governed entirely by the temperature dependence of the solvent viscosity, just as predicted by the hydrodynamic scaling model.[22,23] D_p scales with temperature as T/η_s. For mesoscopic spheres in partly neutralized low-molecular-weight poly(acrylic acids), $D_p\eta_s/T$ is virtually independent of T.

Reducing our earlier measurements[10] to fixed $T - T_g$ rather than fixed T is unnecessary, because it will have no effect on previous conclusions. In particular, the finding that D_p depends on matrix polymer concentration as

$$D_p = D_{p0} \exp(-\alpha c^{\nu}) \qquad (12)$$

remains supported. The hypothesis that eq 12 reflects variations in a glass temperature is rejected by our data. Namely, when we change $T - T_g$ by changing T, D_p shows no dependence on polymer (rather than solvent) properties.

Supplementary Material Available: Tables and plots of D_p vs T/η_s for 0.038-μm polystyrene latex spheres in pure water, 0.1 M NaCl, 2/3-neutralized PAA, 2/3-neutralized PAA:NaCl, and 2/3-neutralized PAA:H_2O. Also given are the linear and quadratic models for D_p based on eqs 10 and 11 (52 pages). Ordering information is given on any current masthead page.

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Registry No. PAA (homopolymer), 9003-01-4; PS (homopolymer), 9003-53-6.