exists) must occur at temperatures below the T_g and the LCST above the decomposition temperatures of the blends and hence they both remain experimentally inaccessible.

Registry No. PEA, 9003-32-1; PVPR, 25035-84-1; heptane, 142-82-5; benzene, 71-43-2; toluene, 108-88-3; methyl propionate, 554-12-1; acetone, 67-64-1; methyl ethyl ketone, 78-93-3; ethyl acetate, 141-78-6; ethyl propionate, 105-37-3; chloroform, 67-66-3; 1,2-dichloroethane, 107-06-2; chlorobenzene, 108-90-7; ethanol, 64-17-5.

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Probe Diffusion in Solutions of Low Molecular Weight Polyelectrolytes

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ABSTRACT: Probe diffusion coefficients (D) of polystyrene spheres ($0.019\ \mu\mathrm{m} \le R \le 0.38\ \mu\mathrm{m}$) were observed in solutions of neutralized and nonneutralized poly(acrylic acid)s ($5\ \mathrm{kDa} \le M_w \le 470\ \mathrm{kDa}$). Correlations were obtained between D and the probe radius, the background polymer's molecular weight, concentration (c), and degree of neutralization, and the solution ionic strength (I) and viscosity (η). D generally follows a stretched exponential $D = D_0 \exp(-\alpha c^\nu I^\beta)$. At low concentrations of nonneutralized polymer, D instead follows $D \sim 1 - kc^{1/2}$. Relations between M, α, ν, and γ are presented.

Introduction

The diffusion of polymer chains and globular probe species through polymer solutions is a complex phenomenon affording substantial information about polymer dynamics. Besides its current theoretical interest, polymer–probe interdiffusion occurs under many physical circumstances. For example, cell cytoplasm is a concentrated (~25 wt % solids) solution of aqueous polymers, almost all of which are polyelectrolytes. The inactive transport of proteins, metabolites, and other materials within the cell provides a natural example of probe diffusion in a concentrated polyelectrolyte system.

An effective approach for studying polymer diffusion is

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to apply quasi-elastic light-scattering spectroscopy (QELSS) to selected ternary polymer–polymer–solvent and polymer–particle–solvent systems. In selected systems, one polymer (the "matrix" or "background" polymer) is isorefractive with the solvent, so that its concentration fluctuations scatter virtually no light, even if its concentration is high. The other ("probe") polymer or particle species is chosen to have a large optical contrast, so it dominates the solution's light scattering. If a dilute probe species dominates scattering by a matrix–probe–solvent solution, theory[1-4] indicates that QELSS obtains the self-diffusion coefficient (D_s) of the probe in the unseen matrix–solvent mixture. In a few cases,[5] some relaxations appear to arise from mutual diffusion of the nonscattering matrix polymer, but no current theoretical model lets matrix polymer modes appear if scattering arises from a *dilute* probe species.

QELSS from ternary random-coil polymer solutions was fruitfully studied by Wheeler et al.,[6,7] Nemoto et al.,[8,9] Martin,[10] Smith et al.,[11] and Amis et al.,[12,13] among others. The motion of globular probes through polymer solutions was originally studied by Laurent and Persson,[14] Turner and Hallett,[15] Brown and Stilbs,[16] Langevin and Rondelez,[17] and Jamieson et al.[18] and more recently studied by Brown and Rynden[19,20] and Russo et al.[21] At elevated matrix concentrations, matrix–probe interactions give D_s with a strong concentration dependence, which has variously been described with power laws[22]

$$D \sim M^{\gamma} c^{\nu} \tag{1}$$

or stretched exponentials[23]

$$D = D_0 \exp(-\alpha c^{\nu}) \tag{2}$$

the latter form being obtained by Adler and Freed[24] with a mean-field approximation and by Phillies et al.[25,26] with a self-similarity approximation.

Prior experiments[27] found a phenomenological expression for globular probe particles

$$D = D_0 \exp(-a c^{\nu} M^{\gamma} I^{\beta} R^{\delta}) \tag{3}$$

where c, M, I, and R are the matrix polymer's concentration and molecular weight, the solution ionic strength, and the probe radius, respectively. Here a, ν, γ, β, and δ are scaling parameters. D_0 is the probe diffusion coefficient in pure solvent. For probe species whose R depends on c, there is evidence[7,28] that D_0 is the D that the probe would have if the matrix polymer could be replaced with pure solvent without changing R. The I^{β} term appears only in polyelectrolyte systems.[29]

Phenomenologically,[27,29] ν is generally in the range 0.5–1, β is roughly −0.8 or −0.9, and $\delta \sim 0$ for neutral polymers, but $\delta \sim 0.3$ or 0.5[33] with polyelectrolyte solutions. From data on a variety of matrix polymers, γ was estimated at 0.8 ± 0.1; a recent study[30] using homologous matrix polymers with fully characterized molecular weight distributions finds $\gamma = 0.82$. Some theoretical arguments[25,26] predict eq 3 for tracer diffusion of neutral random-coil polymers through a random-coil matrix. These arguments, which make reasonably accurate numerical predictions for ν, γ, and a for random-coil polymers, compete with other models of polymer dynamics.[22,31,32]

Probe diffusion in neutralized polyelectrolytes at elevated I was studied by Gorti and Ware;[33] Lin and Phillies[34-36] report on probe diffusion in nonneutralized polyelectrolytes in a solvent containing no added salt. At very low I, anomalies appear in QELSS spectra of polymer solutions;[37,38] these phenomena are not the focus of this paper. We previously[29] reported on probe diffusion by polystyrene spheres in solutions of poly(acrylic acid) (PAA). D was adequately described by eq 3. Because studies were only made with 470-kDa PAA, the M dependence of D was not observed. The polymer neutralization ranged from 0% to 100%; 0–0.1 M NaCl served as the supporting electrolyte. Auxiliary measurements of the solution viscosity (η) showed that the Stokes–Einstein equation does not predict D for small ($R \leq 0.8$ μm) probes surrounded by moderate concentrations ($c = 4.7$ g/L) of two-thirds-neutralized 470-kDa PAA, probe particles diffusing faster than expected from η and R. Adding supporting electrolyte reduces but does not eliminate non-Stokes–Einsteinian behavior.

This paper investigates the effect of matrix molecular weight (M) on D_s in solutions of low-M poly(acrylic acid). D of polystyrene spheres was observed as a function of probe radius, matrix molecular weight and concentration, and solution ionic strength. The next section summarizes our experimental methods. Further sections present experimental findings on probe particles in solutions of neutralized and nonneutralized PAA. A final section compares our results with the literature. Complete data appear in the supplementary material.

Experimental Section

Methods were virtually identical with those of our previous study.[29] Probe diffusion coefficients were obtained with quasi-elastic light-scattering spectroscopy, using He–Ne and Ar$^+$ laser light sources, 90° scattering angle, and RCA 7265 photomultiplier tubes as detectors. Samples were held at 25 ± 0.05 °C. Data was taken by using 64- and 144-channel digital correlators. Spectral base lines (B) were obtained both from delay channels on the correlator and by a priori calculation using the P^2/N method; base lines obtained by these two methods agreed to better than 0.1%.

Spectra were analyzed by using Koppel's methods of cumulants,[39] fitting spectra $S(\mathbf{k},t)$ by weighted linear least squares to

$$\log\,[S(\mathbf{k},t) - B] = \sum_{i=0}^{N} K_i (-t)^i / i! \tag{4}$$

for $1 \leq N \leq 5$. Spectral signal-to-noise ratios, S/N (the ratio of K_0 to the root-mean-square error in fitting eq 4), were in the range 300–1000. An N of 2 or 3 almost always gave a good representation of the data. Known limits on cumulant analysis, based on computer Monte-Carlo simulations of 150 000 spectra,[40] were enforced. For the correlators employed here, these limits restrict cumulant analysis to spectra in which the variance

$$V = 100 K_2^{1/2} / K_1 \tag{5}$$

is less than 65%. This restriction was almost never significant; in most cases, V was around 40%. At our S/N, the error in D due to photon-counting noise is around 0.3%,[40] which is substantially smaller than the scatter arising from sample-to-sample reproducibility.

The poly(acrylic acid)s (Poly-Sciences, Inc.) used as matrix polymers had nominal molecular weights of 5, 90, 150, and 450 kDa. Polymer concentrations were determined with potentiometric titration. In most of this work, polymers were partially or completely neutralized with NaOH; when employed, the added (background) electrolyte was NaCl. Solution indices of refraction were measured with an Abbe refractometer, reported D's being corrected for the solution index of refraction when appropriate. Solution viscosities (η) were obtained with a thermostated Cannon-Fenske viscometer.

Molecular weight distributions of the larger poly(acrylic acid)s were determined with aqueous size-exclusion chromatography, using a column with an efficiency of 3900 plates/m, and differential refractometer and low-angle laser-light-scattering detectors. Analog data from both detectors were digitized to obtain the concentration and the weight-average molecular weight ($M_w(v)$) of each elution volume. Integration of $M_w(v)$ gives the conventional molecular weight averages M_n and M_w (Table I; supple-

Table I
Molecular Weight Distributions of the Poly(acrylic acid)s Used in This Study[a]

M	M_n	M_w	M_w/M_n
90	90.8	282	3.11
150	60.9	238	3.91
450	132	469	3.55

[a] M is the nominal molecular weight; M_n and M_w are measured molecular weight averages; all molecular weights are in kilodaltons.

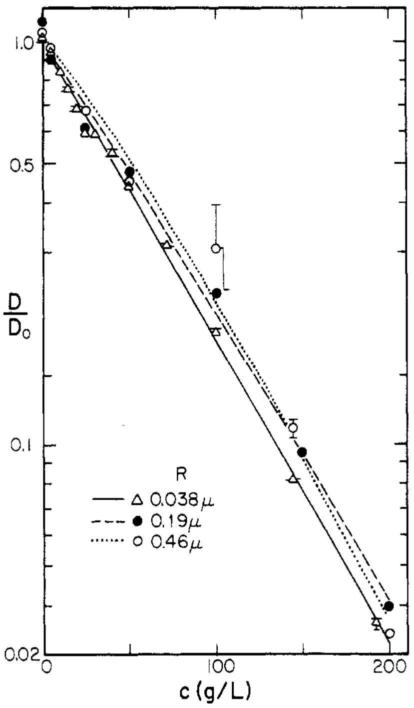

Figure 1. D/D_0 against concentration for polystyrene spheres of indicated radii (legend) in 0.1 M NaCl: two-thirds-neutralized 5-kDa poly(acrylic acid). Solid and dashed lines are fits to eq 2 with D_0, α, and ν as free parameters.

mentary Figure 1). Chromatographic dispersion makes a small artifactual increase in these averages.

Probe particles were carboxylate-modified polystyrene latex spheres (Seradyne, Inc.; Polysciences, Inc.). Most work used spheres with a nominal radius of 0.038 μm; some studies were performed using spheres with nominal radii of 0.19, 0.26, 0.46, and 0.7 μm. In all experiments, probe concentrations were well under 1×10^{-3} w/v, so probe–probe interactions and multiple scattering effects were negligible.

Under our optical conditions, scattering by polystyrene sphere probes completely dominates scattering by the matrix poly(acrylic acid). In addition to previously reported experiments supporting this interpretation,[29,34–36] we studied 90-kDa PAA solutions (for c up to 50 g/L), comparing under identical optical conditions solutions that did or did not contain added spheres. Adding spheres increased the amplitude of $S(\mathbf{k},t)$ by 200-fold. Using sphere-containing solutions as a reproducible external standard, we found that $S(\mathbf{k},t)$ of sphere-free solutions (besides being virtually independent of t) is virtually independent of PAA concentration; i.e., our background intensity arises primarily from stray light and cell window flare, not from the solution. [This is not to say that we cannot measure spectra of PAA–water. By use of 100× laser power and 10× integrating times, reasonable spectra of PAA in water are obtained.]

Results

Neutralized Polymers. We attempted to observe probe diffusion by six different sphere species in solutions of 5-kDa PAA. One sphere species was completely unstable and rapidly flocculated. Two other species were superficially stable; however, their spectral variances increased substantially (to V of 60% or larger) at large polymer concentration. The increase in V suggests the formation of sphere aggregates. At elevated c, D/D_0 of the two species with large V trended well below D/D_0 of the other three species, also suggestive of aggregation. For the three stable sphere species (nominal diameters 0.038, 0.19, and 0.46 μm), V was largely independent of c.

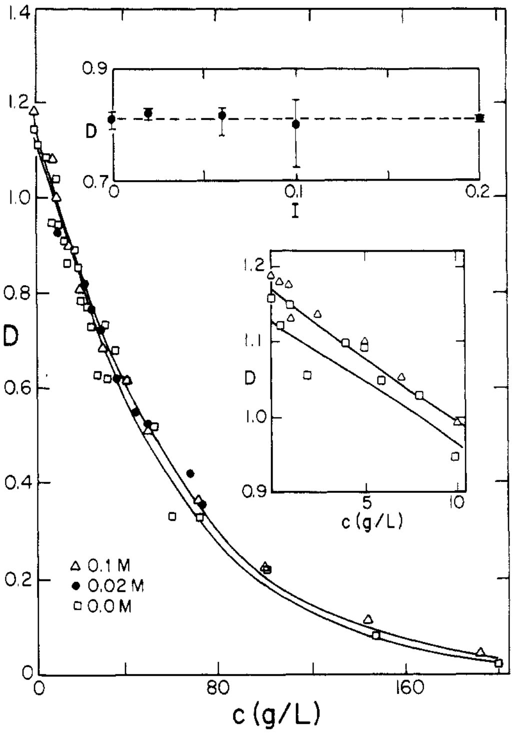

Figure 2. Diffusion of 0.038-μm polystyrene spheres in aqueous two-thirds-neutralized 5-kDa poly(acrylic acid) at ionic strengths of 0, 0.02, and 0.10 M, showing D is virtually independent of I even at 200 g/L of PAA. Lower inset: D against c of PAA at low c. Upper inset: D against I at 20 g/L of PAA, exhibiting the independence of D and I. Lines are from eq 2; see text.

Figure 1 and supplementary Tables 1–3 show D/D_0 for the stable spheres in poly(acrylic acid)–water, two-thirds neutralized, $I = 0.1$ M, for PAA concentrations $0 \leq c \leq 200$ g/L. At 200 g/L of PAA, D is 50-fold less than in pure water. The concentration dependence of D is virtually independent of R, data for the different sphere sizes being almost superposable. Figure 2 and supplementary Tables 4 and 5 compare D of the 0.038-μm spheres in 5-kDa PAA–H_2O at $I = 0.1$, 0.02, and 0.0 M. The concentration dependence of D is the same at each I. The upper inset in Figure 2, which shows results on spheres in 20 g/L of PAA and $0 \leq I \leq 0.205$ M NaCl, confirms the lack of dependence of D on I. In contrast, previous studies[29,33] on probes in high molecular weight polyelectrolytes found that D increases with increasing I at elevated c.

The lines in Figures 1 and 2 represent nonlinear weighted least-squares fits to a stretched exponential (eq 2) with D_0, α, and ν as free parameters. Other fits were made to eq 2 with D_0 held constant and with ν held to its theoretical[25,26] low-M limit, $\nu = 1$. With the 0.038-μm spheres, eq 2 describes the data with an root-mean-square error of 4% or so. Parameters from the analysis appear in Table II.

We also studied spheres diffusing in solutions of nominal 150-kDa poly(acrylic acid) at a variety of ionic strengths, neutralizations, and concentrations. The I dependence of D is shown by Figure 3 and supplementary Tables 6–9, which present D for two-thirds-neutralized PAA at concentrations of 0.1, 1.0, 5.0, and 20 g/L.

Figure 3a and supplementary Table 6 show D of 0.038-μm spheres in 0.1 g/L of 150-kDa PAA as a function of

Table II
Nonlinear Least-Squares Fits of Equation 2 to D of Polystyrene Latex Spheres in 5-kDa Poly(acrylic acid), Two-Thirds Neutralized[a]

I	R, μm	D_0	α	ν	%RMSE
0.0	0.038	1.13	1.26×10^{-2}	1.078	6.6
	0.038	1.18	1.86×10^{-2}	[1.00]	7.4
0.02	0.038	1.17	2.00×10^{-2}	0.94	4.3
	0.038	1.17	1.60×10^{-2}	[1.00]	4.6
0.10	0.038	1.17	1.52×10^{-2}	1.02	3.7
	0.038	[1.20]	1.69×10^{-2}	[1.00]	3.9
0.10	0.19	0.177	1.29×10^{-2}	1.04	8.6
	0.19	[0.200]	1.67×10^{-2}	[1.00]	11.6
0.10	0.46	0.080	7.74×10^{-3}	1.15	13.6
	0.46	[0.085]	1.66×10^{-2}	[1.00]	15

[a] I = solution ionic strength (added NaCl); R = probe radius; D_0, α, ν = fitting parameters from eq 2; %RMSE = percent root-mean-square error in the fit to the data. The brackets "[...]" indicate a parameter that was constrained to the indicated numerical value rather than being floated.

solution ionic strength (I). At this polymer concentration, spheres are not stable in solutions having $I \geq 0.06$ M, clear signs of flocculation being apparent. Below this ionic strength, the spheres are stable, spectra being adequately described by a two-cumulant fit with V near 35%. V is independent of I. D falls markedly at very low I, ranging from $D = 1.15 \times 10^{-7}$ cm^2 s^{-1} above $I = 0.001$ M down to $D = 0.88 \times 10^{-7}$ in solutions containing polymer, counterions, but no added salt.

Figure 3b and supplementary Table 7 give the ionic strength dependence of D for 0.038-μm spheres in 1.1 g/L of 65% neutralized PAA. D is virtually independent of I for $I > 0.02$ M; D falls almost 2-fold as I is reduced from 0.02 M to 0. The fall in D is accompanied by an increase in the nonexponentiality of the data. At large I, spectra are adequately described by two-cumulant fits with $V \sim$ 40–45%. As I is reduced below 0.02 M, first three-cumulant and then four-cumulant fits are needed to describe $S(\mathbf{k},t)$ well. For ionic strengths of 0.02–0 M, V increases from 45% to the region 60–65%. The highest observed variances are within the limits for the validity of cumulant analysis.[40]

Figure 3c and supplementary Table 8 show D against I for 0.038-μm spheres in 5 g/L of 150-kDa PAA. The curves for D against I of the 1 and 5 g/L solutions can be superposed by a vertical translation. Reducing I from 0.1 M to 0 reduces D almost 2-fold, from 0.6×10^{-7} to 0.3×10^{-7} cm^2 s^{-1}. $\mathrm{d}D/\mathrm{d}I$ falls monotonically with increasing I. For all these spectra, a two-cumulant fit obtains V of 35%, while a three-cumulant fit obtains V of 45–50%. The two-cumulant fit is statistically favored at large I. As I is reduced, the 3-cumulant fit becomes more favorable, clearly being better below 0.01 M or so.

Figure 3d and supplementary Table 9 again compare D with I, this time for c = 20 g/L. At this polymer concentration, D depends modestly on I, D decreasing by about 20% between $I = 0.1$ M and $I = 0$.

Unlike our results in 5-kDa PAA solution, in 150-kDa PAA solutions D falls substantially as I is reduced. At all c, the drop-off in D becomes substantial near $I = 0.01$ M. Solid lines in Figure 3a–c show fits to

$$D = D_0 \exp(-\alpha I^{\beta}) \qquad (6)$$

using parameters listed in Table III as "Model 1". Here I is the concentration of added NaCl, the nearly immobile PAA molecules and their counterions not being included in I. Measurements at c = 20 g/L show a decrease in D at low I, but with the 20 g/L solutions a wide range of pairs (α,ν) of parameters describe D against I.

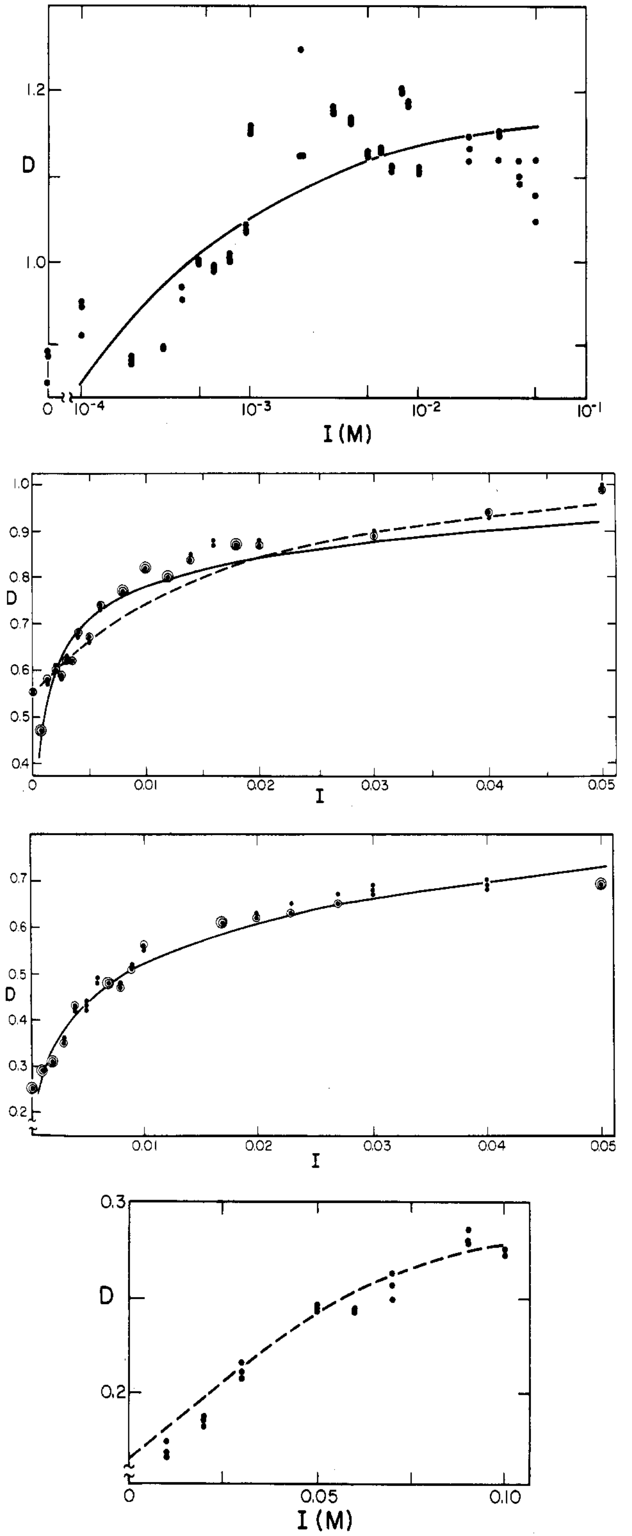

Figure 3. D of 0.038-μm spheres in 150-kDa poly(acrylic acid), 65% neutralized, as a function I. Polymer concentrations were (a) 0.1, (b) 1.1, (c) 5, and (d) 20 g/L. Solid lines represent fits to eq 6. Dashed line in d is a guide for the eye.

Instead of neglecting the sodium polyacrylate (NaPAA) salt when computing I, the individual acrylate groups and their Na$^+$ counterions could be treated as contributing to I as univalent ions having the concentration of the neutralized carboxylic acid residues. Parameters obtained by fitting eq 6 to D, while including the NaPAA in the solution ionic strength, appear in Table III under "Model 2". Fits were made under model 2 with D_0, α, and β as free parameters and with β constrained to the value $\beta = -0.85$ found[29] for probes with 450-kDa PAA. Equation 6, with

Table III
Representations Using Equation 6 of the Ionic Strength Dependence of D of 0.038-μm Polystyrene Latex Spheres in 150-kDa Poly(acrylic acid), Two-Thirds Neutralized[a]

c	D_0	α	ν	%RMSE
		Model 1		
0.1	1.16	−0.0053	−0.447	5.0
0.1	1.157	−0.00326	[−0.5]	5.0
1.0	0.916	−0.0986	−0.31	4.0
5	0.729	−0.658	−0.167	4.3
		Model 2		
0.1	1.146	-2.2×10^{-7}	−2.04	4.0
0.1	1.17	-6.8×10^{-4}	[−0.85]	5.0
1.0	0.92	-6.6×10^{-5}	−1.97	3.4
1.0	0.94	−0.0129	[−0.85]	6.2
5.0	0.75	-1.2×10^{-5}	−3.6	6.8
5.0	0.82	−0.13	[−0.85]	12.3

[a] c = polymer concentration (g/L); D_0, α, β = fitting parameters. Other features as in Table II. Models 1 and 2: see text.

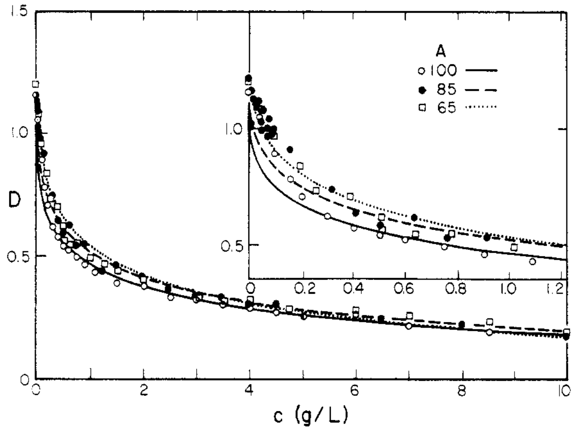

Figure 4. D of 0.038-μm spheres in salt-free 150-kDa poly(acrylic acid), as a function of polymer concentration (c) and percent neutralization (A) of the PAA. Each symbol represents the average of three spectra, the random scatter in D from spectrum to spectrum generally being less than the size of the point. Lines represent eq 2 and parameters from Table IV.

I referring only to added NaCl, is entirely adequate to describe our experiments. Including the NaPAA in I does not reduce the root-mean-square difference between the scaling form and actual measurements. The $\beta = -0.85$ obtained with 450-kDa PAA does not describe well data on 150-kDa PAA solutions; β is M dependent. If I is taken from model 1, $\beta \rightarrow 0$ as $M \rightarrow 0$. With $\beta < 0$, the analytic structure of eq 6 has an essential singularity at $I = 0$, which appears to blur the convergence of the nonlinear least-squares fits.

Figure 4 and supplementary Tables 10–15 examine how polymer neutralization affects the concentration dependence of D. D was obtained for $0 \leq c \leq 10$ g/L PAA and A of 0%, 65%, 85%, and 100%. Data on nonneutralized PAA are treated below. Both 0.038- and 0.26-μm probe particles were employed. There was no added NaCl. The 0.26-μm spheres tend to aggregate if more than 2 g/L of matrix polymer was present; our main emphasis is on the 0.038-μm spheres. As seen in Figure 4, for 0.038-μm spheres the 65% and 85% neutralization points lie on virtually the same curve; increasing A from 85% to 100% reduces D by not more than 10%. Solid curves in Figure 4 represent fits to eq 2; fitting parameters are in Table IV. For $c > 0.2$ g/L, agreement of the data with the stretched exponential form is excellent. Below 0.2 g/L of PAA (inset), the data for each A appear to lie on a straight line, D being larger than expected from the stretched exponential form.

Table IV
Concentration Dependence of D and η of Polystyrene Latex Spheres in 150-kDa Poly(acrylic acid), Based on Equations 2 and 8[a]

R	I	A	D_0 or η_0	α	ν	%RMSE
0.038	0	65	1.31	0.924	0.312	7.2
0.038	0	65	[1.20]	0.828	0.340	8.5
0.038	0	85	1.43	0.966	0.329	6.9
0.038	0	85	[1.20]	0.770	0.386	8.9
0.038	0	100	1.22	0.959	0.299	5.4
0.038	0	100	[1.16]	0.911	0.311	5.5
0.26	0	65	0.210	1.11	0.490	7.5[b]
0.26	0	85	0.223	1.16	0.487	5.9[b]
0.26	0	85	[0.205]	1.07	0.568	6.6[b]
0.26	0	100	0.210	1.21	0.383	5.3[b]
0.038	0.02	65	1.26	0.267	0.695	4.6
η	0.02	65	1.07	0.488	0.593	4.2
η	0.02	65	[1.09]	0.480	0.596	4.2
0.038	0.10	65	1.19	0.196	0.71	4.0
0.455	0.10	65	[0.108]	0.218	0.97	19
0.455	0.10	65	0.121	0.275	0.896	18

[a] R = probe radius (μm); I = solution ionic strength (added NaCl, M); A = polymer neutralization (percent); D_0 or η_0, α, ν = fitting parameters (D_0 in cm^2 s^{-1}, η in cP). Other features as in Table II. [b] Fit for $c \leq 2.0$ g/L.

Table V
Concentration Dependence of η of Nonneutralized Poly(acrylic acid)–Water–No Added Salt at Various Nominal Molecular Weights and Polymer Concentrations, Based on Equation 8[a]

M	η_0	α	ν	%RMSE
90	0.9	0.074	0.728	3.4
150	1.043	0.076	0.679	3.9
450	1.28	0.364	0.503	14.9

[a] M = nominal polymer molecular weight (kDa); η_0, α, ν = fitting parameters from eq 8 (η_0 in cP); parameters constrained to indicated values rather than being floated. Other features as in Table II.

Table V and supplementary Tables 16 and 17 show D for $0 \leq c \leq 20$ g/L of 150-kDa PAA, two-thirds neutralized, at I = 0, 0.02, and 0.1 M. D falls up to 4-fold with increasing c. The solid curves in Figure 5 represent fits to a stretched exponential, the parameters appearing in Table IV. Equation 2 gives a good representation for D at all ionic strengths, except for the aforementioned upward deviation of the data from the curves at $I = 0$ and low c. Unlike probes in 5-kDa PAA (in which D is independent of I) but like probes in 450-kDa PAA[29] or 500-kDa poly(styrene sulfonate),[33] D of probes in 150-kDa PAA depends substantially on I, typically increasing by 2-fold as I is raised from 0 to 0.1 M.

Also indicated in Figure 5 is the fluidity (η^{-1}) of 150-kDa PAA–0.02 M NaCl, showing the familiar result[41,42] that the Stokes–Einstein equation

$$D = \frac{k_B T}{6\pi\eta R} \tag{7}$$

(k_B being Boltzmann's constant, T the temperature, η the solution viscosity, and R the probe radius) is not valid in this solution. Equation 7 errs by as much as a factor of 2, D being larger than expected from R and η. Such obvious artifacts as polymer binding by the probes and polymer-induced probe aggregation would cause D to be smaller than expected from η, the opposite of the observed effect.

Nonneutralized Polymers. Probe diffusion coefficients (using 0.038- and 0.7-μm polystyrene spheres) and viscosities were obtained for solutions of nonneutralized PAA having nominal molecular weights of 90, 150, and 450

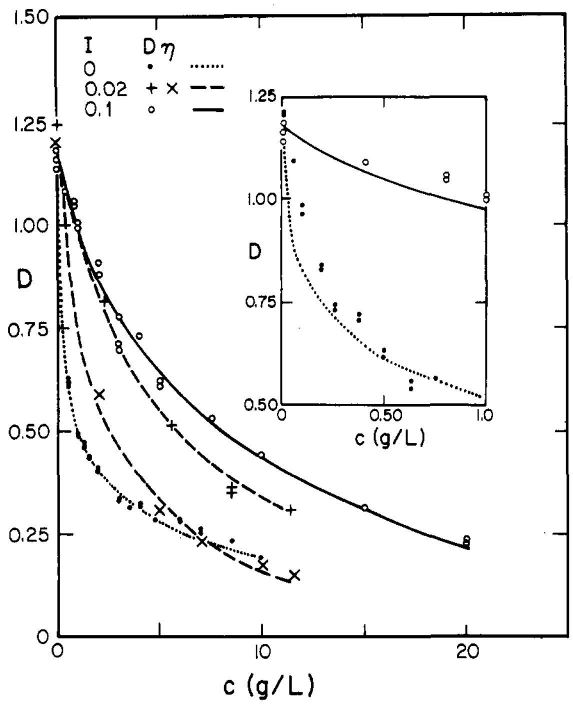

Figure 5. D of 0.038-μm spheres in two-thirds-neutralized 150-kDa poly(acrylic acid) against solution ionic strength. Also, η^{-1} of I = 0.02 M solutions, showing non-Stokes–Einsteinian behavior. Units of η^{-1} are such that η_0^{-1} and D_0 are numerically equal. Solid lines are fits to eq 2 and 8; parameters in Table IV.

kDa. Detailed viscosity measurements for $0 \leq c \leq 50$ g/L appear in Figure 6, supplementary Table 18, and supplementary Figure 18. At large c, measurements of η are described by a scaling form

$$\eta = \eta_0 \exp(-\alpha c^{\nu}) \tag{8}$$

in which η_0, α, and ν are adjustable parameters. [Table V gives η_0, α, and ν from nonlinear least-mean-squares fits.] At low c, η is better represented by

$$\eta = \eta_0(1 + k_2 c^{1/2}) \tag{9}$$

The transition between these domains is illustrated by Figure 6, which describes 90-kDa poly(acrylic acid). Figure 6a compares η with eq 8, which is adequate at large c but imperfect (cf. inset) at small c. Figure 6b plots η against $c^{1/2}$; eq 9 works well below 4 g/L of PAA. Parts C–F of supplementary Figure 18 show corresponding transitions for 150-kDa and 450-kDa PAA solutions. The domains of validity of eq 8 and 9 are separated by a concentration c_η^*. With the 90-kDa and 150-kDa polymers, c_η^* = 10 g/L; with the 450-kDa polymer, c_η^* = 2 g/L.

Probe diffusion measurements on nonneutralized poly(acrylic acid) are represented by Figure 7, supplementary Tables 19–24, and their associated figures. Figure 7a shows D against c for probes in 150-kDa poly(acrylic acid), the solid line being eq 2 using parameters drawn from Table VI. Equation 2 works well at elevated concentrations. At small c

$$D = D_0(1 + k_2 c^{1/2}) \tag{10}$$

gives a better description of D than does eq 2; cf. Figure 7b. Denoting by c_D^* the transition concentration for D between eq 2 and eq 10, we find $c_D^* \approx 4$ g/L for the 90-kDa and 150-kDa polymers, but $c_D^* \approx 2$ g/L for the 450-kDa polymers. c_η^* and c_D^* are difficult to determine exactly. Within experimental precision, at each M we find $c_\eta^* \approx c_D^*$.

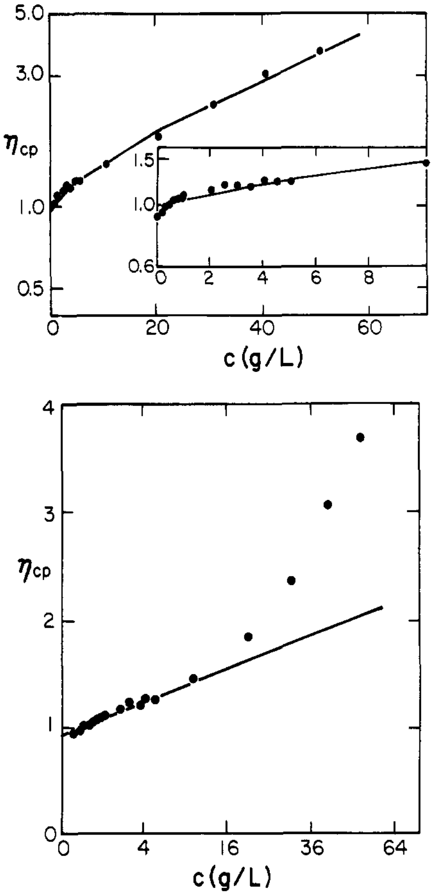

Figure 6. (a) η against c for 90-kDa poly(acrylic acid), no added salt; solid lines represent eq 8. (b) η against $c^{1/2}$, showing η follows eq 9 at $c < c_\eta^*$.

By combining η and D with the Stokes–Einstein equation (7), an apparent hydrodynamic radius (r_H) of the probe particles may be inferred. In 90-kDa and 150-kDa PAA solutions, r_H of the 0.7-μm spheres is virtually independent of c (cf. supplementary Figure 25A,B), while r_H of the 0.038-μm spheres increases from ~180 Å at c = 0 to ~250 Å above c = 10 g/L. This gradual increase in r_H with increasing c, saturating at large c, closely resembles behavior seen in poly(ethylene oxide)–water[41,42] where the increase in r_H with c arises from polymer adsorption by the spheres. Indeed, for 0.038-μm spheres in 90-kDa and 150-kDa PAA solutions, the dependence of r_H on c is well-described by Langmuir adsorption isotherm (curve b in supplementary Figure 25A,B), the layer of bound polymer being ca. 70-Å thick. Adsorption of a 70-Å layer of polymer onto the 0.7-μm spheres would not, within experimental error, change D, so the lack of c dependence of D for 0.7-μm spheres does not prove that 0.7-μm spheres do not bind PAA.

A more complex behavior (Figure 8) is obtained for r_H in solutions of 450-kDa poly(acrylic acid). For both probe sizes, between 0 and 0.8 g/L of PAA, r_H falls by 30%; above 0.8 g/L, r_H rebounds to sizes larger than those obtaining at c = 0. Comparing c of 0 and 50 g/L, for 0.7-μm spheres r_H increases from ~3200 to ~3600 Å, while for 0.038-μm spheres r_H increases from 180 to 420 Å, as might be expected from binding a 250–400-Å layer of PAA. The 30% fall in r_H cannot be due to polymer adsorption, which increases r_H; effects of solution hydrodynamics might, however, reduce r_H. Russo et al.[21] characterize a fall in r_H with rising c as "slip/seining" behavior.

Conclusions

Probe diffusion in polyelectrolyte solutions was studied by Gorti and Ware,[33] who used fluorescence photobleaching recovery to observe fluorescein and fluores-

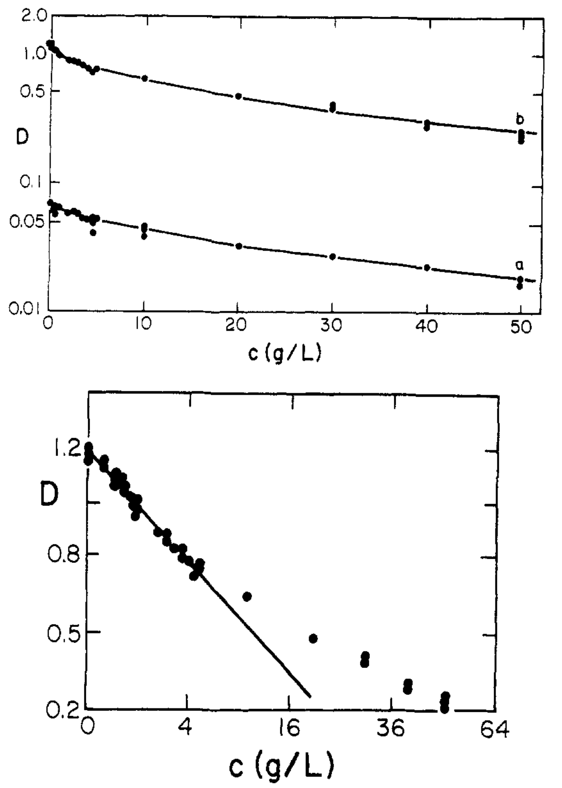

Figure 7. D of 0.038-μm spheres in nonneutralized 150-kDa poly(acrylic acid). (a) Comparison with eq 2, showed stretched-exponential behavior at large c. (b) Comparison with eq 10, showing $c^{1/2}$ behavior at small c.

Table VI
Parameters from Fits of Equation 2 to D of Polystyrene Latex Spheres in Nonneutralized Poly(acrylic acid)–Water–No Added Salt[a]

R	M	D_0	α	ν	%RMSE
0.038	90	1.191	0.246	0.48	4.4
0.7	90	0.0647	0.0599	0.785	4.9
0.038	150	1.196	0.200	0.525	3.4
0.7	150	0.0692	0.110	0.639	3.5
0.038	450	1.421	0.777	0.42	10.0
0.7	450	0.063	0.381	0.539	12.2

[a] Column labels as in Table V.

cein-labeled bovine serum albumin ($R \sim 52$ Å) and polystyrene latex (R $\sim$ 190 Å) in solutions of sodium poly(styrene sulfonate) (NaPSS) of molecular weights 70 and 500 kDa, using solvents with background ionic strengths of 1–50 mM. In these systems, D and η both follow stretched-exponential forms, though with unequal scaling coefficients. The Stokes–Einstein equation is not obeyed, though it is closer to correct for large probes than for small ones. Increasing M or R increases the retardation of a probe by a solution. Gorti and Ware found D/D_0 depends but weakly on I, D falling with increasing I at small c ($c < 4$ g/L) but increasing with increasing I at large c. Probe diffusion of polystyrene spheres in 470-kDa (M_w) PAA solutions was observed by Phillies et al.,[29] whose results were in many respects similar to those of Gorti and Ware: The Stokes–Einstein equation fails, more pronouncedly at large c, small I, and small R than at small c, large I, and large R. D has a stretched-exponential dependence on c and I; at fixed c, D always increases with increasing I. The results here are consistent with these observations.

Our results on probe diffusion in polyelectrolyte solutions are usefully systematized by the scaling equation

$$D = D_0 \exp(-ac^{\nu}M^{\gamma}R^{\delta}I^{\beta}A^{\varpi}) \qquad (11)$$

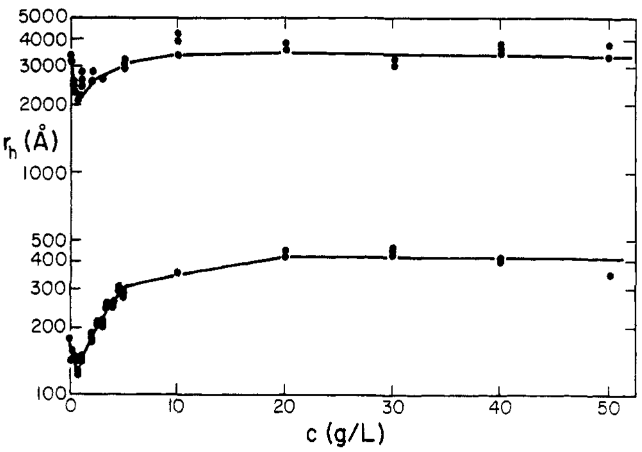

Figure 8. r_H (eq 7) of (a) 0.7-μm and (b) 0.038-μm polystyrene spheres in nonneutralized 450-kDa poly(acrylic acid)–water, I = 0.

A being the polymer neutralization and ϖ its associated exponent.

In solutions of neutralized 5-kDa PAA, eq 11 gives a good account of the c dependence of D. D/D_0 is nearly independent of R and I, so far 5-kDa PAA the scaling exponents β and δ are vanishingly small. Constraining $\nu = 1$ gives good agreement with experiment at all I. We used only two-thirds-neutralized 5-kDa PAA, so ϖ remains undetermined for this M.

In solutions of partially neutralized 150-kDa PAA, eq 11 describes D well. D increases with increasing I, the increase tending to saturate at large I. This behavior is adequately described by taking $\beta < 0$. For c between 0.1 and 5 g/L, β ranges from −0.5 to −1/6, β tending to 0 with increasing c. ν depends on I, increasing from 0.34 to 0.71 between $I = 0$ and $I = 0.1$ M. Polymer neutralization has a weak effect on D, D falling by perhaps 10% as A increases from 0.65 to 1. The data on the effect of A are consistent with $\varpi \approx {}^1/_4$ for ${}^2/_3 \leq A \leq 1$, but ϖ is difficult to estimate accurately.

Our previous study[29] on 450-kDa PAA found D satisfying eq 11 with $\beta \sim -0.8$, $\delta \sim 0.2$, and ν increasing from 0.5 to 1.0 as I increased from 0 to 0.1 M. As A changed from 0.6 to 1.0, D (at c = 1 g/L) fell by perhaps 10%, consistent with $\varpi \approx {}^1/_4$ which is obtained for 150-kDa PAA.

In nonneutralized PAA, eq 11 works well at large c; below 4–10 g/L of PAA, D depends linearly on $c^{1/2}$. Since D and η both show a transition between $A + Bc^{1/2}$ and stretched-exponential behavior at roughly the same c for each M, the failure of eq 11 at low c appears to arise from fundamental solution hydrodynamics. At large c of nonneutralized PAA, where eq 3 is adequate, ν is close to unity, while α increases substantially with increasing M.

Results on 5-, 90-, 150-, and 450-kDa PAA allow treatment of the M dependence of D. From Tables II–VI, α increases sharply with M, as in other polymer solutions.[27] ν falls with increasing M. At low M, the theoretical[25,26] value $\nu = 1$ is observed; at larger M, ν takes quite small values (as low as ${}^1/_3$ for 0.038-μm spheres in two-thirds neutralized PAA solutions), the theoretical limit being $\nu = 0.5$ for large random-coil chains. Figure 9 presents α (obtained by fitting to eq 2) against M_w as taken from our SEC measurements. Data are consistent with $\alpha \sim M^{\gamma}$, γ being the γ of eq 11. For different I, γ ranges between 0.63 and 0.9; the previously observed $\gamma \approx 0.8$ (solid line) gives a good account of the measurements.

Changing M also changes β. The effect of I on D increases substantially with increasing M. In 5-kDa PAA,

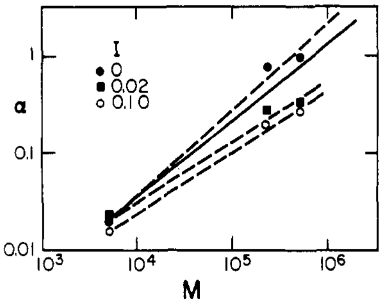

Figure 9. M_w against α for probes in two-thirds-neutralized PAA at different ionic strengths. Dashed lines show $\alpha \sim M^\gamma$ for γ = 0.9, 0.63; solid line is the literature value[30] γ = 0.8.

D is practically the same at I = 0 and I = 0.1 M. With 5 g/L of 150-kDa PAA, increasing I from 0 to 0.1 M roughly doubles D. At the same c, in 450-kD PAA, increasing I from 0 to 0.1 M nearly triples D.[29] Formally, β depends on M_w, ranging from β = 0 at M = 5 kDa to $\beta \sim$ 0.17–0.5 at $M_w \approx$ 250 kDa and $\beta \sim$ 0.9 at $M_w \approx$ 470 kDa.

Viscosities were obtained for the nonneutralized PAA solutions and for the 150-kDa PAA, two-thirds neutralized, I = 0.02 M. In low-M nonneutralized PAA, r_H is independent of c for large probes but increases with increasing c for small probes, the c dependence of r_H being adequately described by Langmuir adsorption isotherms. In low-M PAA solutions, the Stokes–Einstein equation is thus apparently valid, some polymer adsorption by the probes taking place. In 450-kDa PAA, r_H first falls and then rises as c rises, similar effects being seen with 0.038- and 0.7-μm probes.

Previous applications of stretched exponentials to polymer self-diffusion,[23] viscosity, sedimentation, and rotational diffusion[44] are subject to the criticism that α at fixed M is markedly scattered, individual values deviating from the theoretical trend line $\alpha \propto M^1$ by up to a factor of 3. Table II reveals a major source of this scatter, namely that a small (≤10%) error in fixing ν can cause a 2-fold error in α. With ν as a free parameter, we obtain α values scattered over $7.74 \times 10^{-3} \leq \alpha \leq 2.00 \times 10^{-2}$. With the same measurements of D, ν = 1 as an imposed constraint, and I = 0.10, we find α = 0.0168 or 0.0169. Over the range $0 \leq I \leq 0.10$ M, with ν forced to equal 1, α is confined to $1.60 \times 10^{-2} \leq \alpha \leq 1.86 \times 10^{-2}$. Constraining ν = 1 marginally degrades root-mean-square errors while greatly reducing the scatter in α. This behavior is a sensitivity effect. Noise in the data leads to noise in α and ν. A change in ν has a much larger effect on eq 2 than does a change in α, so in fitting noisy data one typically finds small changes in ν being compensated by large changes in α. In numericoanalytic terms, the fitting errors are correlated, the error ellipse being highly eccentric.

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Registry No. PS, 9003-53-6; PAA, 9003-01-4; PAA·Na, 9003-04-7.

Supplementary Material Available: Figure 1 showing the molecular weight distributions of poly(acrylic acid), Tables 1–5 listing diffusion coefficients and variances of polystyrene latex spheres at different concentrations of poly(acrylic acid), Tables 6–9 listing the diffusion coefficients of polystyrene latex spheres at different ionic strengths, Tables 10–17, 19–21, 23, and 24 listing diffusion coefficients of polystyrene latex spheres at different concentrations of poly(acrylic acid), Table 18 listing the viscosities of solutions of poly(acrylic acid), Figure 18 showing viscosity versus poly(acrylic acid) concentration, Figures 20, 22, and 24 showing diffusion coefficient versus poly(acrylic acid) concentration, and Figure 25 showing the apparent hydrodynamic radius versus poly(acrylic acid) concentration (45 pages). Ordering information is given on any current masthead page.

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