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Probe Diffusion in Poly(acrylic acid)–Water. Effect of Probe Size

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ABSTRACT: The diffusion coefficient of carboxylate-modified polystyrene latex spheres of radii 204 Å to 1.5 μm in water–poly(acrylic acid) was measured with quasi-elastic light scattering spectroscopy. At high polymer concentrations ($c > 30$ g/L), D and the viscosity were both described by functions of the form $\exp(-ac^{\nu})$; nonlinear least-squares fits were all consistent with $\nu \cong {}^{2}/_{3}$. With the smaller spheres, polymer adsorption to a thickness of 100–150 Å was apparent. Contrary to some theoretical expectations, the Stokes–Einstein relation $D = k_BT/6\pi\eta r$ fails at high rather than low polymer concentrations, for the largest, not the smallest, spheres. The observed decrease in the apparent hydrodynamic radii of the larger spheres, to values less than those observed in pure water, cannot be due to polymer adsorption but is readily understood in terms of shear thinning of a non-Newtonian polymer solution over the time and distance scales sampled by our probes.

I. Introduction

In previous papers, we have reported studies of the diffusion of various dilute probe species in simple and complex solvents. Of particular interest was the dependence of the diffusion coefficient D on temperature and solvent viscosity. In pure water[1] and in mixtures[2] of water and small-molecule species (glycerol and sorbitol) the diffusion coefficient of polystyrene spheres and bovine serum albumin agreed well with the Stokes–Einstein equation

$$D = k_BT/f = k_BT/6\pi\eta R \qquad (1)$$

Here, f is the drag coefficient, η is the macroscopic viscosity, separately measured, and R is the hydrodynamic radius of the probe species in pure water. Mixtures were studied over the temperature range 5–50 °C; η ranged from 0.8 to 1000 cP.

For small molecules in solvents with $\eta > 10$ cP, it is well-known[3,4] that D and the electrophoretic mobility λ are proportional to η^{-a}, with $0.63 < a < 0.7$, as opposed to the $a = 1$ implied by the Stokes–Einstein equation. We were therefore motivated to use light scattering spectroscopy to study probe diffusion as the probe and solvent molecules became comparable in size.[5] Rather than trying to use ever-smaller probe particles, we used poly(acrylic acid)–water as the (mixed) solvent; by this expedient, some of the solvent molecules were made similar in size to the probe particles. This is not an unprecedented idea. For example, Hallet and Gray[6] and Turner and Hallet[7] report on the diffusion of polystyrene spheres through solutions of biopolymers. The index of refraction increments of polystyrene and poly(acrylic acid) in water are such that almost all of the light scattering arises from the polystyrene spheres.

As the polymer concentration was increased, the Stokes–Einstein equation (1) failed to predict the diffusion coefficient of the probes. Equation 1 was modified, defining the apparent hydrodynamic radius r_0 by

$$D = k_BT/6\pi\eta r_0 \qquad (2)$$

where D and η are the measured values of the diffusion coefficient and the viscosity. r_0 is a way of parameterizing the diffusion coefficient and is not necessarily related to the physical size of the probe particles. (Equivalently, one could reinterpret eq 2 by identifying η as the microviscosity experienced by the diffusing particles.) When the solvent composition was held fixed, eq 2 accurately predicted the temperature dependence of D. However, r_0 increased substantially with increasing polymer concentration.[5]

A variety of other experimental[8–14] and theoretical[15] studies have been made of particle motion through polymer and biopolymer solutions. In some of these,[8] changes in f with increasing polymer concentration have been interpreted in terms of binding of polymer molecules by the probe particles, the adsorbed layer of polymer contributing to the true hydrodynamic radius R. In other studies, changes in f have been interpreted in terms of direct and hydrodynamic interaction between polymers and probe species, the polymer molecules acting by changing the effective viscosity of the solvent.[9–14] A variety of empirical and theoretical relations between D and c have been propounded, as discussed in section IV.

In this paper, our previous studies on the temperature dependence of a single probe, in polymer solutions of various concentrations, are extended to examine how the diffusion coefficient depends on the radius of the probe. The solvent used was salt-free nonneutralized poly(acrylic acid), molecular weight 300 000, in water. Comparison is made with various empirical and theoretical forms for the concentration dependence of D and with the expected shape of adsorption isotherms.

Experimental methods are treated in section II. Section III gives the experimental results. The discussion and conclusions are presented in section IV.

II. Experimental Methods

Poly(acrylic acid) (MW = 300 000) was purchased commercially (Polysciences, Inc.) as a 25 wt % solution. Individual water–polymer mixtures were made by a dilution of the poly(acrylic acid) with 14-MΩ deionized water, to final concentrations of 1.13×10^{-2}, 3.62×10^{-2}, 0.113, 0.245, 0.467, 1.13, 2.45, 3.62, 4.67, 7.47, 11.3, 16.9, 25.1, 35.4, 47.6, 58.8, 75.3, 97.1, 123, and 145 g/L. The actual polymer concentration in each mixture was determined by titration with NaOH. The pH of the yet-to-be titrated, salt-free solutions ranged from 5.45 at a concentration of 1.13×10^{-2} g/L polymer to 2.54 at 47.6 g/L and 2.24 in the 145 g/L solution.

The probe particles used in this work were carboxylate-modified polystyrene latex spheres of nominal diameters 0.038 μm (Dow Scientific; surface charge density 0.296 mequiv of CO_2^-/g of polymer), 0.15 μm (Polysciences, Inc.; 0.92 mequiv of CO_2^-/g of polymer), 1.28 μm (Polysciences, Inc.; 0.12 mequiv of CO_2^-/g of polymer), and 3.0 μm (Polysciences, Inc.; 0.12 mequiv of CO_2^-/g of polymer). The hydrodynamic radii of these spheres, inferred from their measured diffusion coefficients in pure water, were 204 Å, 800 Å, 0.62 μm, and 1.5 μm, respectively. Sphere solutions

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for the light scattering spectroscopic studies were prepared directly in the light scattering cells (which were glass fluorimeter cells, four sides polished) by mixing small amounts of the stock sphere solutions with previously filtered solutions of poly(acrylic acid). The sphere concentrations were 5×10^{-4} (w/v) for the 204-Å spheres and 1.3×10^{-5} (w/v) for the larger spheres. Because the sphere concentrations were so small, sphere–sphere interactions, including sphere–sphere electrostatic interactions, are virtually nonexistent. The diffusion of the spheres may therefore be attributed entirely to sphere–solvent interctions. Furthermore, at such low sphere concentrations, multiple scattering is negligible.

All hydrodynamic studies were performed at 24.9 °C. Solvent viscosities were measured with Ubbelohde and Cannon-Fenske viscometers, measurements of η being reproducible to better than 1%. Diffusion coefficients were measured with quasi-elastic light scattering spectroscopy, following ref 7. The correlator time base was set so that the correlation time (the $1/e$ time) corresponded to 7–25 correlator channels. The actual time per correlator channel varied from 10 μs (for the 204-Å spheres dissolved in 1.13×10^{-2} g/L poly(acrylic acid) to 0.02 s (for the 1.5-μm spheres in the 123 g/L polymer solution).

Spectra were analyzed by the method of cumulants, spectra being fit to the form

$$\tfrac{1}{2} \ln \left[S(k,t) - B\right] = \sum_{i=0}^{n} (-t)^i K_i / i! \qquad (3)$$

The value of n that gave the best fit in the statistical sense depended on the sphere size. For solutions containing 204-Å spheres, 80% of the spectra gave the best fit with $n = 3$. For the larger spheres, roughly equal numbers of spectra were fit best with $n = 1$ or with $n = 2$. The root-mean-square error in the fit also depended on the size of the spheres. The root-mean-square error found in the best fits for the 204- and 800-Å-sphere solutions was about 0.5% of the spectral amplitude at $t = 0$, the latter number being obtained from the cumulant K_0. In solutions of the 0.62- or 1.5-μm spheres, root-mean-square errors averaged 1.3% of the $t = 0$ spectral amplitude.

To calculate the scattering vector

$$k = (4\pi n/\lambda) \sin(\theta/2) \qquad (4)$$

(here λ is the laser wavelength in vacuo and θ is the scattering angle), the index of refraction n of each polymer solution was determined with a Bausch and Lomb Abbe-56 refractometer.

No difference was detected between the diffusion coefficient of spheres in freshly prepared samples and the same sphere suspensions after standing for 4–8 h. In our polymer solutions, the polystyrene spheres thus do not aggregate over the period of times used in our experiments.

In very viscous solutions, there exists the possibility of inadvertent heterodyne detection of the scattered light, due to hypothesized microbubbles introduced during the mixing of the spheres with the polymer solutions. To test for heterodyning, a glass melting-point capillary was introduced into the scattering cell as a local oscillator. The diffusion coefficients obtained with heterodyne and homodyne spectroscopy were in good agreement.

With the larger spheres in the more concentrated polymer solutions, there arose the risk that the decay times might have become too long to be observed, even with the largest sample time that our correlator can provide. A preliminary estimate of the needed sample time was made for each sphere size, using the Stokes–Einstein equation and the solution viscosity to estimate a coherence time

$$\tau = (2Dk^2)^{-1} \qquad (5)$$

and requiring that the 56 data channels of the correlator span roughly five coherence times. This requirement precluded study of the largest spheres in the most concentrated solutions. With this precaution, reasonable spectra were obtained.

The polymer–water solutions, without added probe particles, scatter very little light. The light scattering spectra of the water–poly(acrylic acid) solutions were negligible (<1%) by comparison with the scattering due to the spheres.

The diffusion coefficient of polystyrene latex spheres has been reported to depend significantly on pH. The diffusion coefficient of each size of sphere, in pure water, was therefore determined over the pH range 2.2–6.0; no dependence of D on pH was observed.

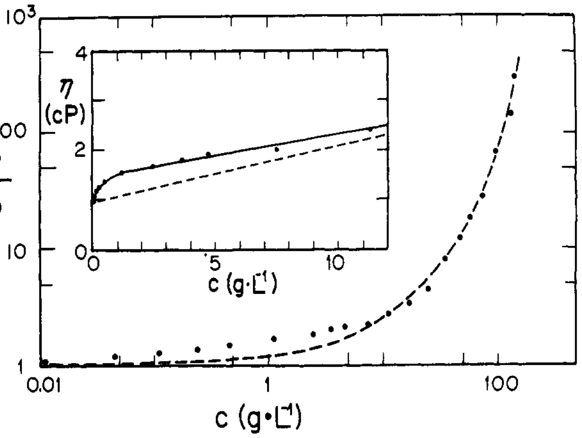

Figure 1. log–log (and, in the inset, linear–linear) plot of the viscosity of poly(acrylic acid)–water as a function of polymer concentration. The dashed line is from a two-parameter fit to eq 6; the solid line was drawn to guide the eye.

III. Results

The concentration dependence of the viscosity of the water–polymer mixtures is shown in Figure 1. The viscosity increases sharply with increasing polymer concentration, going from 0.96 cP (for the 1.13×10^{-2} g/L solution) to 270 cP (in the 145 g/L solution). On careful examination, η does not have a simple exponential dependence on concentration. As may be seen in the inset to Figure 1, over the range 0–10 g/L the viscosity first rises sharply with increasing concentration and then levels off.

The diffusion coefficient of each size of sphere was determined in pure water and in each of the mixed solvents. The best estimates of the hydrodynamic radii of the spheres in pure water were 204 Å, 800 Å, 0.62 μm, and 1.5 μm, respectively. Data on the polystyrene spheres in the polymer solutions are shown in parts a–d of Figure 2, which give D/D_0 for each size of sphere as a function of polymer concentrations. The nominal values of D_0 used to generate Figure 2a–d were 1.13×10^{-7}, 3.1×10^{-8}, 3.88×10^{-9}, and 1.17×10^{-9} cm^2/s. Measured diffusion coefficients ranged from 9.88×10^{-8} cm^2/s for the 204-Å spheres in 1.13×10^{-2} g/L poly(acrylic acid) to 2.38×10^{-11} cm^2/s for the 1.5-μm spheres in 123 g/L poly(acrylic acid).

As may be seen in Figure 2, the reproducibility in values of D is worse for large sphere sizes and higher polymer concentrations. For polymer solutions less concentrated than 25 g/L, the average spread in D was ±3–7%; in the more concentrated polymer solutions, random fluctuations in a series of measurements of D ranged from 7 to 16%. The 1.5-μm spheres in the presence of large amounts of poly(acrylic acid) gave the worst results. The increase, at higher polymer concentrations, in the error in D may be attributed to the reduction in the duration (in units of the correlation time) of individual measurements of the spectrum.

The variance v gives information on the deviation of a spectrum from a single-exponential form. The 204-Å, 800-Å, and 0.62-μm spheres in pure water showed v in the range 30–40%; the 1.5-μm spheres are somewhat more polydisperse, showing variances in the range 60–70%. In order to obtain a meaningful numerical value of the variance, free of errors resulting from the truncation of the cumulant expansion after a finite number of terms, one needs at least a valid third-order fit of the spectrum to a cumulant series. Our measurements are therefore more qualitative than quantitative in nature. For the 204-Å and

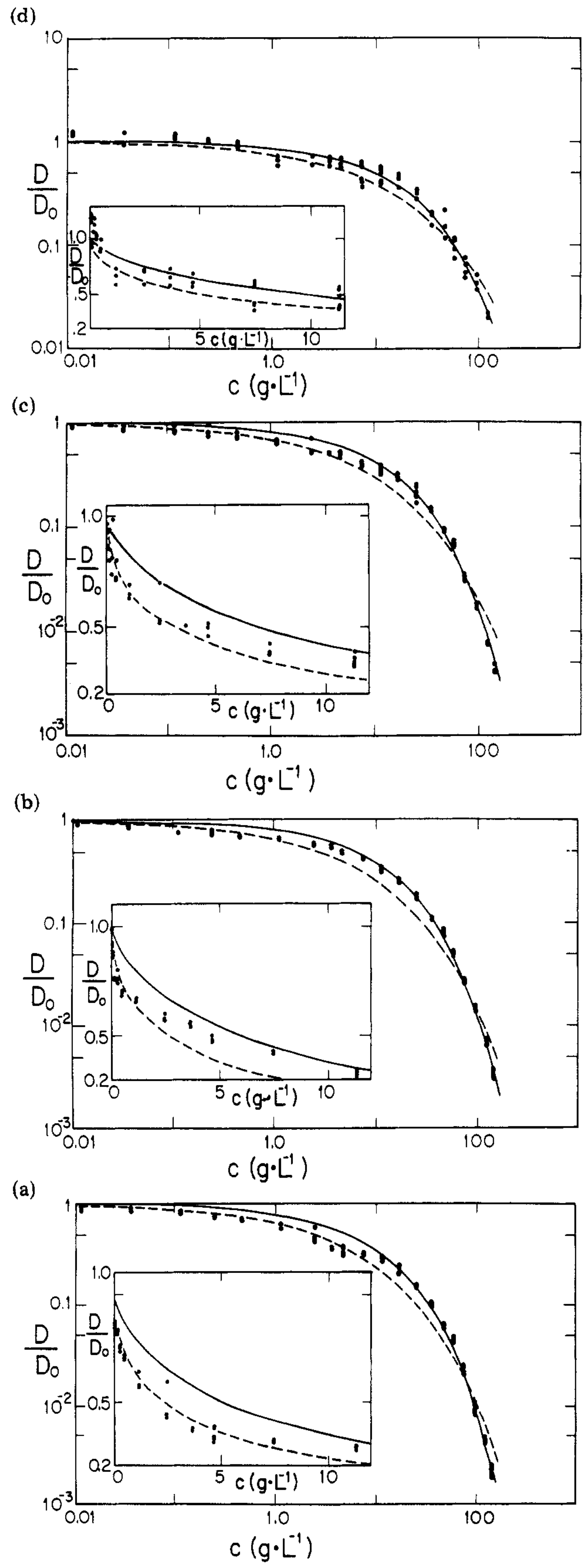

Figure 2. log–log (and, in the insets, linear–linear) plots of the diffusion coefficient of polystyrene spheres of radius (a) 204 Å, (b) 800 Å, (c) 0.62 μm, and (d) 1.5 μm as a function of poly(acrylic acid) concentration. Lines were obtained from nonlinear least-mean-squares fits to eq 7 (solid line) and 8 (dashed line); fitting parameters are given in Table I.

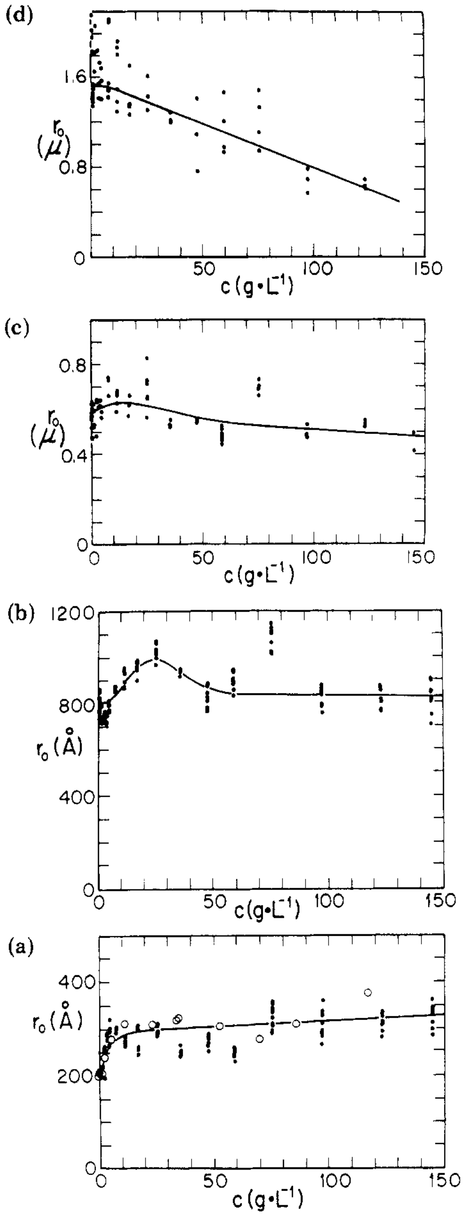

Figure 3. Apparent hydrodynamic radius r_0 calculated from the product of measurements of D and η, as given in eq 2 and the data in Figures 1 and 2 for polystyrene spheres of radius (a) 204 Å, (b) 800 Å, (c) 0.62 μm, and (d) 1.5 μm. Open circles (a) are apparent hydrodynamic radii of the 204-Å spheres, as inferred in ref 7 from the temperature dependence of D. Solid lines are drawn to guide the eye.

1.5-μm spheres, v increases sharply (perhaps by 30 percentage points) as the polymer concentration is raised from 0 to 5 g/L. For the 800-Å and 0.62-μm spheres with polymer concentrations much below 100 g/L, v does not depend on polymer concentration by an amount outside of its (substantial) random scatter; at polymer concentrations above 100 g/L, v for these sphere sizes may tend to increase.

D and η may be combined by use of the Stokes–Einstein equation (2) to calculate the apparent hydrodynamic radius r_0 of the spheres in each solution. Results are shown in Figure 3; Figure 3 also includes the apparent hydrodynamic radius of the 204-Å spheres at 15 °C and other temperatures.[7] For the 204-Å spheres, r_0 increases by roughly 50% between 0 and 10 g/L; r_0 may increase again at higher concentrations, but by little more than the experimental error. The apparent radius of 800-Å spheres increases by about 25%, peaks at a polymer concentration near 30 g/L, and then falls off again. The apparent radius of the 0.62-μm spheres is weakly dependent on polymer concentration, falling by around 0.1 μm between pure water and the most concentrated solutions. The 1.5-μm spheres appear to shrink substantially, perhaps by as much as a factor of 2, as the polymer concentration is increased.

IV. Discussion

The application of scaling-type concepts to the theory of polymer solutions suggests that the viscosity may be described, at least within a single concentration regime, by a power-law form

$$\eta/\eta_0 = e^{ac^{\nu}} \tag{6}$$

η_0 being the solvent viscosity. A nonlinear least-mean-squares fit of our data to eq 6, made with a grid searching procedure, found $a = 0.168$ and $\nu = 0.706$. The dashed line in Figure 1 is the curve generated from these values for a and ν. At concentrations above 30 g/L, the agreement between experiment and the phenomenological curve is adequate, the average disagreement between theory and experiment being roughly 7%. At polymer concentrations below 30 g/L, there is a systematic difference between the measured data and the power-law curve, suggesting that in this concentration range a simple power-law form is not appropriate. The systematic difference between the data and eq 6 is emphasized in the inset to Figure 1, which is a linear plot of η against c. The measured viscosity is as much as one-third greater than the value predicted by eq 6. Furthermore, experiment reveals a break point in the η–c plot near 0.5 g/L concentration; the phenomenological equation does not include such an effect.

The clear break in the η–c plot near 0.5 g/L might be interpreted as a crossover concentration, at which there is a change from one sort of solution behavior to another. As noted by de Gennes et al.[16] for a salt-free polyelectrolyte, the transition concentration c^* between the so-called dilute and semidilute regions is very small. For the neutral polymer poly(ethylene oxide)[13] of MW = 300 000, one has $c^* \sim 0.3$ g/L. The discontinuity in slope near 0.5 g/L may therefore represent c^* in our system. However, a polyelectrolyte solution is characterized by a variety of lengths, including the radius of gyration, the persistence length, the hydrodynamic screening length, and the Debye length, so some other transition concentration might lie near 0.5 g/L.

Almost all macromolecular fluids show at relatively low shear rates a non-Newtonian dependence of the viscosity η on the shear rate r.[17-20] The shear rate in a capillary viscometer, of the sort used in these measurements, is of order 10 s^{-1}. A more detailed study of the viscosity of nonneutralized poly(acrylic acid) solutions was not made.

It has been found experimentally[9,10,12] that the motion of compact particles through a polymer solution sometimes follows a scaling-type formula

$$D/D_0 = S/S_0 = e^{-ac^b} \tag{7}$$

where a and b are substance-dependent parameters, S is the sedimentation coefficient, and the subscript zero denotes quantities measured in pure solvent. Ogston et al.'s model of a gel[15] predicts

$$D/D_0 = e^{-aRc^{1/2}} \tag{8}$$

for the diffusion of a sphere through a fixed latticework of rigid rods, where a is a constant independent of the size of the probe.

Table I
Numerical Results for Diffusion Coefficients Fit to the Concentration of Poly(acrylic acid)

	$D/D_0 = \exp(-ac^b)$		$D/D_0 = \exp(-\alpha' C^{1/2})$
	a	b	α'
204 Å	0.236	0.65	0.454
800 Å	0.208	0.66	0.426
0.62 μm	0.184	0.67	0.385
1.5 μm	0.151	0.67	0.300

Langevin and Rondelez[13] ascribe the scaling form

$$D_0/D = f/f_0 = \psi(R/\xi) \tag{9}$$

to de Gennes, Pincus, and Velasco,[21] ξ being a mesh distance in the entangled polymer chains, R being the probe radius, f being the drag coefficient, and ψ being an unspecified function. If one has

$$\xi \sim c^{-\nu} \tag{10}$$

eq 7–9 are consistent. Theoretical arguments indicate $\nu = {}^3/_4$ for neutral polymers[16] and $\nu = {}^1/_2$ for polyelectrolytes.[22]

Experimental values for the exponent ν depend on both the probe species and the polymer solution. ν was found to be 0.62 for silica particles (Ludox) in poly(ethylene oxide)–water,[13] 0.52 for bovine serum albumin in poly(ethylene oxide)–water,[13] 1 for carboxylated butadiene spheres in dextran solutions,[23] and ${}^1/_2$ for various probes in hyaluronic acid.[9,12]

To compare with the above, a nonlinear curve-fitting scheme was used to compare our experimental data on D/D_0 to eq 7 and 8. The quantity minimized was

$$\sum_i [\ln (D_i/D_0) + ac_i^{\,b}]^2 \tag{11}$$

the sum being over data points and b being either fixed at ${}^1/_2$ or used as a free parameter. Numerical results of this procedure are given in Table I and shown in Figure 2. In the figure, the dashed lines correspond to $b = {}^1/_2$, while the solid lines correspond to b being a free parameter.

At polymer concentrations below 3–5 g/L, eq 8 represents the data on all four sphere sizes reasonably well, agreement being worst for the 800-Å spheres. In solutions with higher polymer concentration, there are clear systematic differences between eq 8 and the data. In the intermediate concentration range (5–80 g/L), eq 8 predicts too small a value for D. At higher polymer concentrations, eq 8 predicts too large a value of D. Thus, at concentrations above 5 g/L, ln (D/D_0) does not scale as $c^{1/2}$.

The failure of eq 8 at high polymer concentrations might have been expected from the model that this equation represents. Equation 8 is based on the assumption that polymer chains are rigid rods. While plausible when few rods are present, at high concentrations there will be electrostatic screening by the rods and their associated ions. If electrostatic interactions are screened by other polymer molecules, distant points on the same rod will be noninteracting; the polymer molecule will be flexible, though perhaps with a long persistence length.

At concentrations above 10 g/L, the difference between the measured data and eq 7 is quite small; indeed, it is little larger than the scatter in the data points. At concentrations below 10 g/L, eq 7 is inadequate to describe the motions of the smaller (204 Å, 800 Å, and 0.62 μm) spheres; measured diffusion coefficients are appreciably smaller than eq 7 would predict. For all particle sizes, the constant b is consistent with the simple fraction ${}^2/_3$. A similar result was ($b \sim 0.52 \pm 0.2$ to $b \sim 0.65$) found by Langevin and Rondelez for various probe particles in poly(ethylene oxide) solutions. While b does not depend appreciably on the probe species, the constant a decreases with increasing probe diameter.

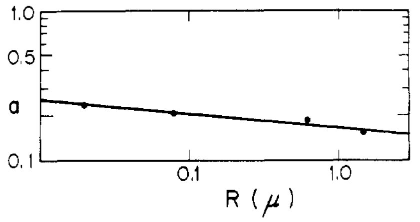

Figure 4. Dependence of the parameter a, eq 7, on the sphere size. A least-mean-squares fit (line) indicates $a \sim R^{\delta}$ for $\delta = -0.09$.

Equations 7–10 suggest that D/D_0 might depend on probe size as

$$D/D_0 = e^{-a'R^{\delta}c^{\nu}} \tag{12}$$

This prediction is tested in Figure 4, in which log a is plotted against log R.· Within the not-insubstantial scatter of the data points, log a is linear in log R. The slope of the line indicates $\delta = -0.09$.

On the basis of eq 9, Langevin and Rondelez[13] give the form

$$S/S_0 = \exp[-(R/\xi)^{\delta}] + \eta_0/\eta \tag{13}$$

for the concentration dependence of the sedimentation coefficient. For dilute solutions of stable particles, s/s_0 and D/D_0 should be the same. This form was constructed so as to give the desired behavior of s/s_0 in two asserted limits:

First, if $R \gg \xi$, it was asserted that the diffusing probe should perceive the solvent essentially as a continuum. In this case, Stokes' law in the form of Walden's rule should apply

$$S/S_0 = \eta_0/\eta \tag{14}$$

Equation 1 goes to this limit if R is increased at fixed concentration. If one were to change ξ by changing c, the detailed behavior of eq 13 would depend on the concentration dependence of the viscosity.

Second, if $R \ll \xi$, it was asserted that the particle should effectively be retarded by the viscosity of the solvent and not the viscosity of the solution, so $D \approx D_0$. Equation 13 gives this limit if $R/\xi \ll 1$.

One emphasizes these two limits were set a priori, and not on the basis of experimental measurement or detailed molecular-hydrodynamic theory. In general, eq 13 indicates that the apparent hydrodynamic radius r_0 of a large particle in a concentrated polymer solution will be equal to its nominal hydrodynamic radius R in pure solvent. Small probe particles in low-concentration polymer solutions (i.e., c sufficiently small that $\xi \ll R$, but $c > c^*$) are predicted to diffuse more rapidly than indicated by the Stokes–Einstein equation, so their apparent hydrodynamic radii in the presence of the polymer will be less than their hydrodynamic radius in pure solvent.

Our experimental findings do not agree with these predictions. The apparent hydrodynamic radius of our larger probe particles, for which $R \gg \xi$ is always satisfied, does not follow the Stokes–Einstein equation: r_0 does not equal R at all polymer concentrations. Instead, at small c wer find $r_0 \approx R$, while, at larger c, r_0 *falls* with increasing polymer concentration. Furthermore, at small c the apparent hydrodynamic radius of our smaller probe particles increases smoothly with increasing polymer concentration. (As we do not have an independent measurement of ξ in this system, we cannot be certain that our probes are small enough that $R \ll \xi$ is ever satisfied.) Not surprisingly, a brute-force effort to fit our data to eq 13, either for fixed R or for fixed c, gave strange results.

Our interpretation of our data is as follows: The increase in the radius of the 204-Å spheres for $0 \leq c \leq 10$ g/L is simply interpreted as an adsorption isotherm; cf. ref 8. At low polymer concentration, the spheres are partially coated with polymer, so that r_0 increases with increasing polymer concentration and increasing polymer binding. If the polymer concentration is high enough, the sphere surfaces are saturated with polymer; no more adsorption occurs. As the polymer concentration is increased, the effective hydrodynamic radius of the 204-Å spheres increases to roughly 320 Å. At polymer concentrations above 5 g/L no further change in r_0 is seen. These measurements are consistent with the formation of a layer of adsorbed poly(acrylic acid) of limiting thickness 100 ± 20 Å on the 204-Å spheres. Variations in D in solutions with >5 g/L polymer are no different from the variation in the fluidity η^{-1} of the solution; this behavior of D would be observed if the layer of adsorbed polymer had a constant thickness and if eq 1 described D. In the absence of evidence as to its density, the concentration/area of the bound polymer cannot be deduced from our data.

Polymer adsorption by the 800-Å spheres could explain the initial increase in the radius of those spheres. By comparison with the 204-Å spheres, the binding maximum is reached at a higher polymer concentration (25 g/L); furthermore, the maximum thickness of the bound layer is larger (approximately 200 Å). Since one needs a higher activity of polymer to saturate the spheres, and since the thickness of the bound polymer layer is larger (suggesting that the polymer makes larger loops between points at which it becomes attached to the spheres), we conclude that the 800-Å spheres are less effective at binding poly(acrylic acid) than are the 204-Å spheres. It seems difficult to explain the decrease in r_0 of the 800-Å spheres for $c >$ 25 g/L in terms of polymer desorption at higher polymer concentration. At higher concentrations, the solutions have lower pH. In more acid solution, fewer of the carboxylic acid groups on the polymers and on the polystyrene spheres will be charged; this change will reduce electrostatic polymer–sphere repulsions and enhance hydrogen bonding, thereby assisting polymer adsorption at higher polymer concentration, the inverse of the observed effect.

Layers of adsorbed polymer, of the thicknesses observed on the smaller spheres, would at best be barely observable in the behavior of the 0.62- or 1.5-μm spheres. An increase of 100 or 200 Å in their apparent hydrodynamic radii would be masked by the scatter in the experimental measurements.

We observe no anomaly (Figure 3a, inset) in the apparent hydrodynamic radius of any of the spheres in the region 0–2 g/L poly(acrylic acid). The transition in the solution properties, evident in the viscosity data, appears to have no effect on the force responsible for the sphere motion, other than to change the viscosity of the system.

It is well-known that the viscosity of a macromolecule-containing fluid becomes non-Newtonian at relatively low shear rates.[18,19] A decrease in viscosity with increasing shear rate (shear thinning) is commonly observed; the onset of shear thinning shifts to lower shear rates as the macromolecule concentration is increased. There appears to have been relatively little theoretical work on macroparticle diffusion in non-Newtonian fluids. An equilibrium fluid is not subject to an external shear. However, the shear rate in the immediate vicinity of a Brownian particle, on the time scale of its velocity relaxation time, may be substantial. While an inappropriate value for η will give an inappropriate value, in eq 2, for r_0, present theories of diffusion do not indicate which value for $\eta(r)$ is appropriate for computer r_0. If the extent of shear thinning, on the time and distance scales probed by our larger particles, were greater than any shear thinning which may occur in our viscometers, the anomalous decrease in the apparent hydrodynamic radius of the 0.63- and 1.5-μm spheres, and the inconstant radius of the 800-Å particles, would be explained.

An obvious length scale in our system is the bare radius R of the probe particles. Another obvious length scale is the mean distance l between polymer molecules, which ranges from 3700 Å (at a polymer concentration of 1×10^{-2} g/L) to 270 Å at a concentration of 25 g/L and 150 Å at a concentration of 145 g/L. A plausible supposition is that deviations from the Stokes–Einstein relation, manifested as a decline in r_0 with increasing polymer concentration, can be described with a universal function H of the single parameter R/l

$$r_0 = RH(R/l) \tag{15}$$

Here, l is $C^{-1/3}$, C being the number concentration.

One feature of $H(R/l)$ is the polymer concentrations c^+ at which r_0 begins to fall. For the 800-Å spheres, c^+ is 25 g/L, corresponding to $R/l \approx 3$. This condition on R/l is never met by the 204-Å spheres; the 204-Å spheres show an apparent increase in r_0 at low concentrations but do not show a decrease in r_0, even at the highest polymer concentrations studied. The 0.62- and 1.5-μm spheres would reach $R/l \approx 3$ at concentrations c^+ of 13 and 8 g/L, respectively. A careful inspection of parts c and d of Figure 3 shows that r_0 of the 0.62-μm spheres does have a weak maximum near 13 g/L. While the data on the 1.5-μm spheres is more badly scattered, the data are at least consistent with the assertion that r_0 does not fall until the concentration c^+ of 8 g/L is attained.

Furthermore, were $H(R/l)$ a universal function, those particles with larger R would achieve given values of H at larger l, i.e., at smaller c. Our data show that H is a monotonically decreasing function of c; from the previous sentence's argument, the slope $\mathrm{d}H/\mathrm{d}c$ ought therefore be largest for the particles with largest R, as is in fact observed.

In conclusion, the diffusion coefficients of a series of different carboxylate-modified polystyrene latex spheres were determined in water–poly(acrylic acid) as a function of polymer concentration. With the smallest spheres, the concentration dependence of the apparent hydrodynamic radius could be satisfactorily explained in terms of superficial adsorption of polymer by the spheres. The apparent hydrodynamic radius of the larger spheres falls with increasing polymer concentration; the exact concentration dependence of r_0 depends on the sphere size. The behavior of r_0 is consistent with the occurrence of shear thinning on the time and distance scales probed by the larger spheres, shear thinning being observed when the probe radius are sufficiently larger than the distance between polymer molecules.

A comparison of our diffusion data and some predictions of some scaling-type theories of polymer dynamics showed substantial qualitative disagreement. However, at high polymer concentration D/D_0 and η/η_0 both followed power-law forms (eq 6 and 7). If c^ν is interpreted as ξ^{-1}, our results indicated that for a nonneutralized polymer of a weak acid the exponent ν is approximately $^2/_3$.

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References and Notes

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