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Probe Diffusion in Poly-L-lysine Solution

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ABSTRACT: Probe diffusion of polystyrene (PS) latex particles through semidilute solutions of poly-L-lysine (PLL) has been studied by using the techniques of quasielastic light scattering and sedimentation in the ultracentrifuge. Attention has focused on three questions: whether the same frictional coefficient can be used to describe the motion detected by the two different techniques, how the diffusion scales with polymer concentration and molecular weight, and whether the particle radius (compared with the correlation length of the solution) is an important parameter as recent theories predict. We find that fair agreement is obtained between the two techniques, but where differences occur the frictional coefficient for sedimentation is less than that for light scattering. The behavior of the diffusion coefficient as a function of concentration can be described by a unique curve for all PLL molecular weights, by expressing the concentration in terms of a reduced value C/C^*, where C^* is the critical concentration for coil overlap. This is in accord with the ideas of scaling theory. Finally, the behavior of the two different probe particles used (radii of 490 and 800 Å) did not differ significantly, in contradiction of theoretical predictions but in agreement with other recent experimental studies on probe diffusion.

Introduction

The diffusion of a spherical probe particle through polymer solutions is a phenomenon of widespread interest with applications, for instance, to transport and diffusion in the cytoplasm of a living cell, the drying of paints, oil recovery, photography, and chromatography.

Studies of polymer solutions have largely been motivated by the theoretical models of Edwards[1] and de Gennes.[2] These models divide random-coil polymer solutions into three regimes: dilute solutions (in which the spacing between polymer molecules is much larger than their radius of gyration R_g), semidilute solutions (in which neighboring polymer coils overlap), and concentrated solutions (melt and meltlike solutions dominated by polymer–polymer friction). The concentration separating the dilute and semidilute regimes is represented as C^* and the concentration separating the semidilute and concentrated regions as C^+.

In these models, the polymer self-diffusion coefficient, D_s, in the three regimes is claimed to occur by fundamentally different processes. In dilute solutions, polymer molecules move nearly independently of each other, and diffusion is therefore determined largely by R_g and the properties of the solvent. However, in semidilute and concentrated solutions of high molecular weight polymer, the polymer molecule is greatly hindered by other polymer segments. The concentration dependence of the diffusion coefficient varies with the quality of the solvent.

Our interest in probe diffusion in polymer solutions was inspired by recent work of Phillies et al.[3-10] on the diffusion of colloidal particles in neutral polymer solutions and (more recently) the diffusion of polystyrene latex spheres through solutions of partially neutralized poly(acrylic acid). In the latter case, the diffusion was studied as a function of polymer concentration, pH, ionic strength, and probe radius. They fitted their data to a stretched exponential equation of the form

$$D/D_0 = \exp(-AC^{\nu}I^{\beta}R^{\delta}) \tag{1}$$

Here D_0 is the diffusion coefficient of probe particles in pure solvent and D the equivalent coefficient at polymer concentration C (g/L), I is the ionic strength of the solution, R is the probe radius, and A is a constant of the system. They found ν ranged between 0.5 and 1.0 as a function of concentration. No dependence on R was found; i.e., δ was equal to zero.

In semidilute solution, the diffusion of a probe particle (at very low volume fraction) is considered to be a function of R/ξ, where ξ is the correlation length of the transient network, formed as the polymer molecules overlap above the critical concentration C^*. The Stokes–Einstein relation for the probe particle diffusion, which relates the diffusion coefficient to the viscosity of the solvent, will break down if the microscopic viscosity experienced by the probe particle is not the same as the macroscopic viscosity, which is measured experimentally. This will be the case for diffusion of particles of radius $R \ll \xi$, since the probe will be essentially unaffected by the presence of the polymer during much of its motion. In this case, the appropriate microscopic viscosity is likely to be close to that of the pure solvent. Experiments done by Phillies et al.[9,10] and Gorti and Ware[11] found that the Stokes–Einstein relation did indeed break down. However, even for $R > \xi$, when it might be thought that the Stokes–Einstein law should be obeyed, the experimental data so far available seem to suggest that the law still breaks down, although less dramatically.[10]

The situation is even more complex for a polyelectrolyte because of possible charge interactions and the nontrivial identification of ξ. The correlation length for a polyelectrolyte has been written by Odijk[12] in the form

$$\xi = L_t^{-1/4}\kappa^{1/4}(aC)^{-3/4} \tag{2}$$

where L_t is the total persistence length of the polyelectrolyte chain, κ the Debye–Huckel constant, and a the contour distance between charges on the chain.

The friction experienced by a probe particle in a solution of polyelectrolyte of concentration C is then given by[13] (derived from the expression of Langevin and Rondelez)

$$f/f_0 = [\exp(-R/\xi) + \eta_0/\eta_m]^{-1} \tag{3}$$

where η_m is the macroscopic viscosity of the polymer solution, η_0 is the viscosity of the pure solvent, and ξ is as defined above (eq 2). Equation 3 predicts scaling relationships for the diffusion coefficient in terms of polymer charge density, polymer concentration, solution ionic strength, and probe radius. It also suggests that the microscopic viscosity experienced by the diffusing particle is different from the macroscopic viscosity, and hence a non Stokes–Einsteinian behavior would be expected, in

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accord with the experimental data cited above.

Cukier[14] gave a theoretical treatment for the diffusion of Brownian spheres in semidilute polymer solutions, where the polymer coils are no longer free to move with the solvent. He provided separate derivations for solutions containing polymers of the rod and coil type, the nature of screening in the two types of solutions being different. He found that at sufficiently high concentrations, $C > C^*$, the quantity f/f_0 has a $C^{1/2}$ dependence of the form

$$f/f_0 = \exp(-BRC^{1/2}) \tag{4}$$

Frictional coefficients are involved in both sedimentation and diffusion. If, as in simple solvents, these coefficients are identical, then the combination of sedimentation (S_0) and diffusion (D_0) coefficients yields the well-known Svedberg relationship

$$M = S_0RT/D_0(1 - \bar{v}\rho_s) \tag{5}$$

where M is the molecular weight, $\bar{v}$ the partial specific volume of the diffusing or sedimenting species, and ρ_s the density of the solvent. However, when the solvent contains polymer molecules which occupy a significant volume of the system, then the frictional coefficients will depend on the polymer concentration in a complicated manner due to the direct interaction between molecules, as well as hydrodynamic interactions,[16] and it is quite conceivable that the frictional coefficient in sedimentation (f^*) will differ from that in diffusion (f_m). This problem has been highlighted by recent experimental work[17,20] that has examined the two frictional factors, f^* (from sedimentation measured in an analytical centrifuge) and f_m (from diffusion measurements using photon correlation spectroscopy, PCS).

f^* is related to the sedimentation coefficient (itself defined as the sedimentation rate in unit centrifugal field) by

$$S = \frac{M}{N_A f^*}(1 - \bar{v}\rho_s) \tag{6}$$

where N_A is Avogadro's number and M is the molecular weight of the solute. f_m is related to the dilute solution diffusion coefficient, D, which in this work has been determined exclusively by dynamic light scattering. As pointed out by Rallison and Hinch,[15] such coefficients may be identified with the mutual diffusion coefficient, given by

$$D_m = \frac{C}{N_A f_m}(\mathrm{d}\mu/\mathrm{d}C) \tag{7}$$

where μ is the chemical potential of the solute. In the ideal case, the thermodynamic term disappears and this equation reduces to the Stokes–Einstein form

$$D = k_BT/f_m \tag{8}$$

In addition to the thermodynamic term in the expression for diffusion that is not involved in sedimentation, the effect of any direct molecular interactions may cause f to become frequency/time dependent; that is, the value of f may depend on both the time and the spatial scale on which the measurement of f is made, implying that f^* and f_m may differ. It should be noted that f^* is measured over essentially macroscopic dimensions and times of many seconds, whereas f_m is determined over much shorter distances (~wavelength of light) and times in the millisecond range.

Table I
Properties of Polylysine Samples

M_w	M_w/M_n	C^*, g/L	$[\eta]$	R_g, Å
52 000	1.17	2.3	0.44	205
90 000	1.17	1.1	0.91	315
175 000	1.17	0.46	2.17	525
353 000	1.05	0.18	5.55	910

The present work is concerned with the transport mechanism of polystyrene latex spheres at low volume fractions (serving as probe particles) in semidilute polymer solutions of the polyelectrolyte poly-L-lysine. The probe concentration in these experiments was constant and so low ($\phi = 2 \times 10^{-4}$ for the light-scattering experiments) that thermodynamic terms are not involved (as was verified by comparison of measured diffusion coefficients with those extrapolated to zero concentration). We have sought simple and universal properties of the semidilute polymer regime. By comparing our results with other data in the literature, we hope to provide a clearer picture of transport processes in this regime. The second purpose is to compare the two methods of investigation, the analytical centrifuge and PCS, for our particular system. If the suggestion that f_m and f^* are not equal is correct, then agreement between the two techniques could not be expected. In particular, if the frictional factor depends on time scale, then a lack of correlation between sedimentation and PCS data would be expected.

Experimental Section

Materials. Poly-L-lysine (PLL) was supplied by Sigma as polylysine hydrobromides, with an M_w/M_n ratio between 1.05 and 1.17 and molecular weights varying between 3600 and 353 000 (Table I). Molecular weights less than 52 000 (3600 and 22 000) induced flocculation even at low polymer concentrations and therefore could not be used for this study and are not included in Table I.

PLL was dissolved in triply distilled water with no added salt. At the pH value (~7) thus obtained, PLL is essentially an extended coil. The concentration range used was between 0.5 and 20 g/L, which covers the overlap concentration C^* for all molecular weights, as will be shown below. As mentioned above, the solutions were prepared without any added salt, and therefore their ionic strength varied with the polymer concentration. Assuming complete ionic dissociation for the two concentrations, 2 g/L of PLL M_w = 90 000 and 20 g/L of the same polymer, the concentration of free bromide counterion would be 10^{-2} and 10^{-1} M, respectively. The corresponding change in the ionic strength would affect the value of ξ. However, at the pH values in the present experiment, ~7, dissociation is significantly reduced by ion pairing,[21] and changes in ionic strength would be much smaller than suggested above. Thus the concentration of free bromide ions quoted above is much overestimated for the case of 2 g/L (probably by at least 50%) and even more so for the 20 g/L concentration.

Weakly charged polystyrene (PS) latex spheres were used, those of 800-Å radius supplied by Dr. J. W. Goodwin and those of 490-Å radius supplied by Agar Aids. The radii were determined by electron microscopy and PCS measurements. The volume fraction of latex spheres used was 2×10^{-4} for the light-scattering experiments and 1×10^{-3} for the sedimentation. These latex spheres were prepared by the persulfate-initiated process and would be expected to have a surface charge density of about 0.2 mequiv/g.

Methods. a. Photon Correlation Spectroscopy. The photon correlation spectroscopy (PCS) instrument used was described earlier.[22] A single-frequency, Spectra-Physics He–Ne 15-mW Model 124A with vertical polarization was used as a light source. The horizontally scattered light from the cell was detected by a photomultiplier (EMT 9863) over the angular range 5–135° with respect to the incident beam. Specially shaped and positioned baffles were used to cut down stray light. The signal from the photomultiplier was led, via a Malvern amplifier–discriminator (RR63), to the Malvern correlator K7025. Digital output from the correlator was stored on a floppy disk and eventually processed on an IBM 3084 computer. The homodyne autocorrelation

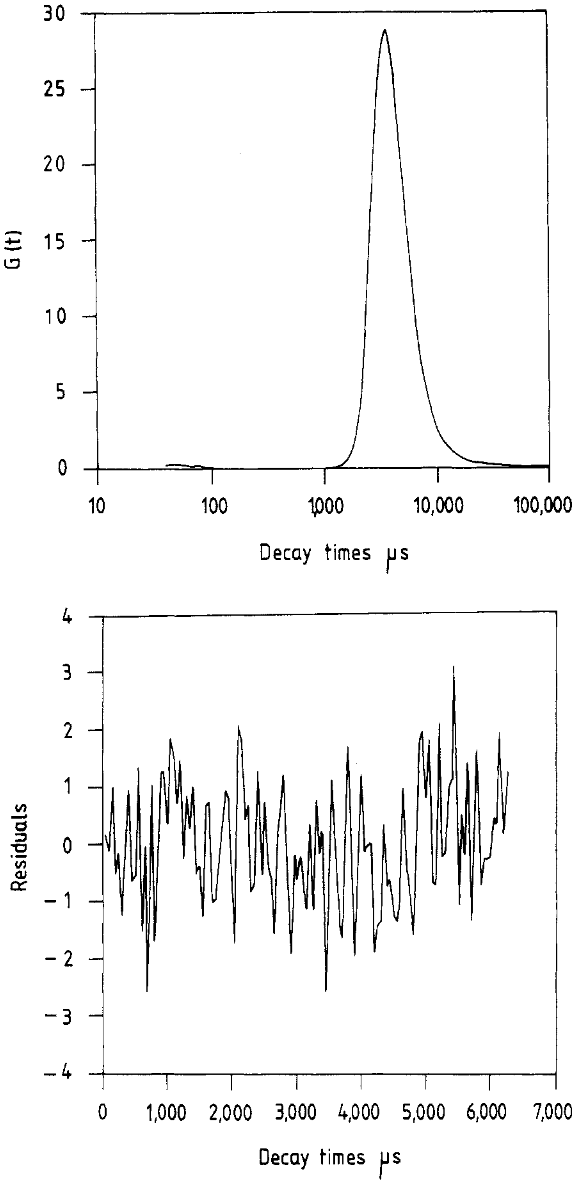

Figure 1. (a, Top) Plot of the distribution of relaxation times of PS latex particles diffusing in PLL solution of 15 g/L concentration as a function of log $\tau = 1/DK^2$; K is the scattering vector. (b, Bottom) Plot of the residuals.

function $g'(t)$ was measured at 25 ± 0.02 °C. The PCS data analysis was principally performed by using a multiexponential fitting program (with 100 exponentials, this being thought to give a near enough approximation to a continuous distribution of relaxation times) based on the maximum entropy method.[23] (Some additional analysis was carried out by using the cumulants method, and fair agreement was found between the two methods.) The maximum entropy method is a very general approach, making no assumptions regarding the scattering material and capable of handling both single and multiple peak distributions as well as broad distributions. It is assumed that the normalized field autocorrelation function is given by

$$g'(t) = \int_0^{\infty} G(\tau)\exp(-t/\tau)\mathrm{d}\tau \approx \sum_{k=1}^{100} G(\tau_k)\exp(-t/\tau_k) \qquad (9)$$

where t is time, τ is decay time given by $\tau = 1/Dk^2$ (k being the scattering vector), and $G(\tau)$ is the distribution function of decay times. The output of the IBM computer gave a plot of $G(\tau)$ against τ (on a logarithmic scale). In this work, this plot was a well-defined peak at all PLL concentrations (including zero), with occasionally a small well-separated second peak due to aggregation. Typical results are shown in parts a and b of Figure 1, the latter being a plot of the residuals (calculated as in ref 23) as a function of decay time. For each run, the diffusion coefficient was calculated from the decay time corresponding to the maximum in the distribution. The value for each PLL concentration was determined by taking the average of 10–15 experimental values. The error in the final D value was estimated to be about 2%.

b. Sedimentation Velocity. Sedimentation velocity experiments were performed in a Beckman Model E machine equipped with diagonal schlieren optics and a RITC temperature-measuring facility. The speed was measured to be 12 950 rpm ± 0.5%, at which no significant sedimentation of PLL occurred. Further, at this speed heating effects during centrifugation were small (≈0.2 °C/h), so that the mean temperature was known to 0.05 °C. Since the density difference between latex particles and solvent was very small, no attempt to control the rotor temperature by the usual heating coil and refrigeration was made, since this tends to introduce temperature gradients and effects due to convection. Instead, the temperature was allowed to rise naturally, and runs were performed at about 20 °C. Sedimentation coefficients were then corrected to the same PLL solution at 25 °C.

The viscosity term (η_t/η_{25}) in this correction procedure may be written in the form

$$\frac{\eta_t}{\eta_t^{\circ}}\,\frac{\eta_{25}^{\circ}}{\eta_{25}}\,\frac{\eta_t^{\circ}}{\eta_{25}^{\circ}}$$

where the superscript ° refers to pure water. Here the first two terms are relative viscosities at temperatures t and 25 °C, respectively, and the last term represents the changing viscosity of water. Experimentally, it was found that the relative viscosities of the polymer solutions were independent of temperature over the ranges used, so that the last term only remained. It was obtained from published tables. The experimental sedimentation coefficients obtained, S_t, were therefore corrected to 25 °C by the following modification of the usual equation:

$$S_{25} = \frac{(1-\bar{v}\rho_{25})}{(1-\bar{v}\rho_t)}\,\frac{\eta_t}{\eta_{25}}S_t \qquad (10)$$

where $\bar{v} = 0.95$ was assumed. The scatter of experimental points was significantly larger than for well-defined proteins and virues of size comparable with the latex particles. This probably reflects the small density difference between the particles and solvent, as well as a residual tendency to aggregation.

Sedimentation experiments have one important advantage over PCS techniques in that the measurement of sedimentation coefficients is a direct technique that can often cope with nonmonodisperse samples (e.g., when broad or multiple peaks are generated). By contrast, PCS is an "averaging" method for which populations with characteristic times differing by a factor of 2 are not easily resolved. Thus the interpretation of PCS data is extremely difficult if polydispersity (e.g., due to aggregation) is thought to be present to a significant extent. A well-defined peak was usually found in the sedimentation data, although sometimes a small second, well-separated peak also appeared (in this case ignored). Because this could, as indicated above, conceivably lead to problems of interpretation of the PCS data, the larger part of the data has been collected from the ultracentrifuge. A disadvantage of the sedimentation velocity method is the occurrence of the buoyancy term $(1-\bar{v}\rho_s)$ which, by its form, is critically dependent upon the accuracy of $\bar{v}$ and ρ. Thus for $\rho_s = 1.0$, and $\bar{v} = 0.95$, a 1% error in v results in an approximately 20% error in $(1-\bar{v}\rho_s)$. Any variation in v (possibly from adsorption effects) could therefore be troublesome.

Viscosities of PLL solutions of all molecular weights were measured with a calibrated Ostwald viscometer in a constant-temperature bath held at 25 °C. Densities of solutions were determined by the weight of the solution in a pycnometer of known volume.

Analysis of Results. The sedimentation and diffusion of the latex particles in water over a range of low concentrations (up to 1 g/L) were first studied, from which extrapolation to zero latex concentration could be performed. These values are subject to some uncertainty since charge effects are present which will be reported in a further publication.[24] A low concentration ($\phi = 1 \times 10^{-3}$) was then chosen (as suitable for studying the effect of dissolved PLL) at which the sedimentation and diffusion coefficients were close to those at zero concentration of latex. Sedimentation and diffusion coefficients were then measured at PLL

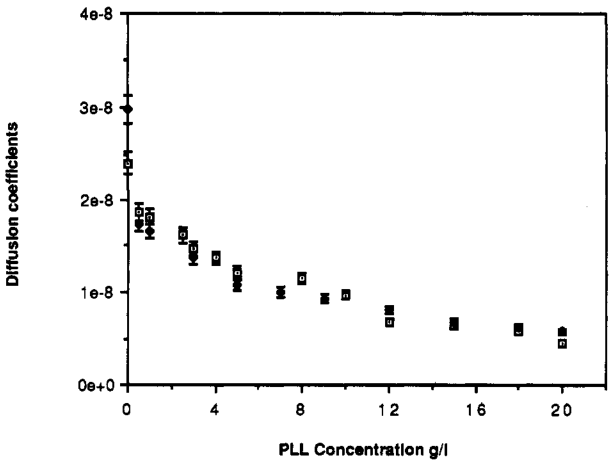

Figure 2. Plot of diffusion coefficient for PS probe particles of radius 800 Å as a function of PLL concentration. M_w of PLL = 90 000 g/mol: (▣) D calculated from sedimentation experiments; (◆) D determined by PCS.

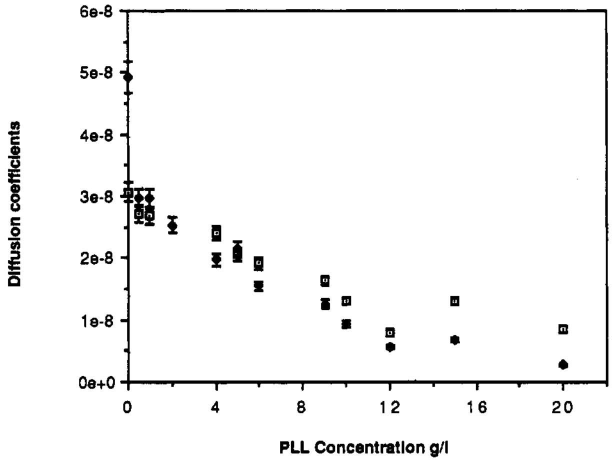

Figure 3. Plot of diffusion coefficient for PS probe particles of radius 490 Å as a function of PLL concentration. M_w of PLL = 90 000 g/mol: (▣) D calculated from sedimentation experiments; (◆) D determined by PCS.

concentrations of up to 30 g/L, allowing extrapolation to zero PLL concentration (constant latex concentration). Writing $M/N_A = {}^4/_3\pi R^3\rho_p$ in eq 6 yields

$$f^* = \frac{4}{3}\pi R^3 \frac{\rho_p - \rho_s}{S} \qquad (11)$$

Equation 11 permits f^* values to be calculated from sedimentation coefficients (corrected to 25 °C via eq 10).

In eq 11, ρ_p and ρ_s are the densities of the particle and solution, respectively. ρ_p was taken to be 1.0520 ± 0.0002 g cm^{-3} as reported by Cheng and Schachman.[25] Solvent densities ρ_s were measured over a range of polymer concentrations, giving a smooth line through the data points; required density values were interpolated from this line. Typically, ρ_s was 1.0021 ± 0.0004. With such a low value of $\rho_p - \rho_s$, a small error in either ρ value results in a large uncertainty in $\Delta\rho$ and therefore in f^*.

A calculated diffusion coefficient, D_{calc}, could then be found from eq 8 and 11 by using f^* in place of f_m in eq 8. In this procedure, no assumptions about the nature of the viscosity are involved. However this approach allows a direct comparison of whether D_{calc} and the measured D are comparable and hence indicates whether the same frictional coefficient/viscosity is appropriate in the two cases.

Results

A comparison of the measured and computed ($D_{calc} = k_BT/f^*$) values of the diffusion coefficient is plotted as a function of PLL concentration at pH 7.2 in Figures 2 and 3 for probe particles of 800- and 490-Å radius, respectively.

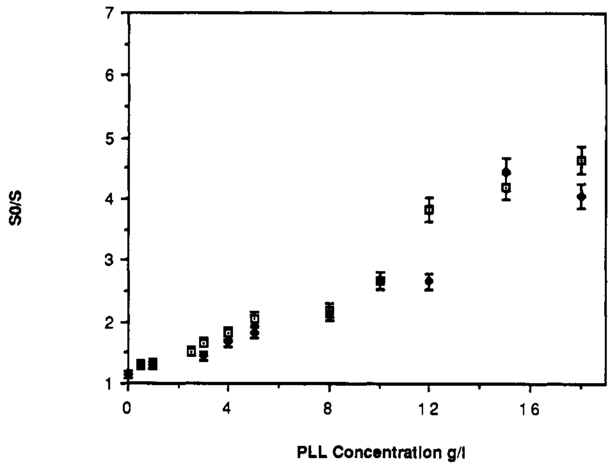

Figure 4. Plot of reduced sedimentation coefficient S_0/S (corrected to 25 °C) as a function of PLL concentration. M_w of PLL = 90 000 g/mol: (▣) S_0/S of PS probe radius 800 Å; (◆) S_0/S of PS probe radius 490 Å.

It can be seen that for the larger particles good agreement is obtained throughout, but for the smaller particles a discrepancy between the two curves becomes significant at higher concentration, the values calculated from sedimentation being systematically higher. This effect will be discussed more fully elsewhere.[24] It should be noted that adsorption of the PLL to the probe particles occurs (even at low PLL concentrations), which will increase the actual hydrodynamic radius of the particle. This is probably responsible for the abrupt fall in D on passing from zero PLL concentration to the lowest concentration used in this study, at which saturation of the surface has already occurred (saturation occurs at a few milligrams per liter for the latex concentrations used here). This should affect both techniques and therefore will not affect the general conclusions drawn. A detailed discussion of the behavior upon adsorption will be published separately, where it will be shown that an adsorbed layer, ~20 nm in thickness, is formed.

Figure 4 shows a plot of S_0/S versus concentration of PLL for polystyrene latex spheres of the two different radii. It should be noted that S_0/S is not necessarily unity for zero PLL concentration, and this is caused by the particular S_0 value chosen by extrapolation. Both probes are predominantly larger than the average mesh size of the transient polymer network, as will be shown below. The data shown in Figure 4 indicate that, in general, the reduced sedimentation coefficients are independent of probe radius, in contrast to Cukier's prediction of eq 4.

In order to consider the scaling behavior of the sedimentation coefficient, information is needed on the overlap concentration C^* and the mesh size ξ of the transient network of the semidilute solution. This data has been obtained from consideration of the intrinsic viscosity of solutions of different concentration. Fuoss[26] found the following empirical equation for the specific viscosity, η_{spec}, of polyelectrolytes:

$$\frac{\eta_{spec}}{C} = \frac{A}{1 + BC^{1/2}} \qquad (12)$$

On the basis of this equation, Figure 5 shows the plot of C/η_{spec} as a function of $C^{1/2}$ for the different molecular weights. In all cases, a straight line is obtained which, when extrapolated to infinite dilution, gives the reciprocal of the intrinsic viscosity $[\eta]$.

The standard scaling argument[3] proposes that the onset of the semidilute regime should occur at a concentration

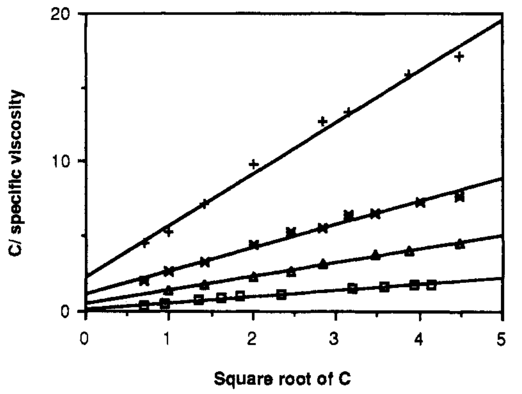

Figure 5. Plot of C/η_{spec} as a function of square root of PLL concentration: (+) PLL M_w 52 000 g/mol; (*) PLL M_w 90 000 g/mol; (△) PLL M_w 175 000 g/mol; (□) PLL M_w 353 000 g/mol.

C^* when the overall concentration is comparable with the local concentration inside a single coil. This leads to the identity[27]

$$C^*\left(\frac{N_A \frac{4}{3}\pi R_g^{\,3}}{M}\right) \sim 1 \qquad (13)$$

(Strictly speaking, this equation will only apply to a flexible polymer, which can be regarded as spherical, and not to a polyelectrolyte, but we will use it to give us an estimate of C^*.)

Flory[28] showed that the bracketed term in eq 13 was proportional to $[\eta]$, with a constant of proportionality of order unity when concentrations are expressed in g/mL. Thus, with $[\eta]$ determined experimentally for the PLL solutions as discussed above, C^* has been calculated as $1/[\eta]$ for each molecular weight and R_g also calculated from eq 13. These values for R_g, C^*, and $[\eta]$ are tabulated in Table I for the four different molecular weights used. While it is recognized that there are various assumptions, explicit or implicit, in this procedure, we feel it does provide a useful working approximation for these parameters; C^* cannot be regarded as a well-defined quantity, although its physical meaning is quite clear.

From the values for R_g in Table I, the scaling of the radius of gyration with molecular weight can be obtained. A plot of the limited data available from this study (Figure 6) shows that the effective exponent for the molecular weight is 0.78, i.e.

$$R_g \sim M^{0.78} \qquad (14)$$

This value for the exponent seems entirely reasonable, suggesting that the charges on the chain cause extension, so that the radius of gyration is larger than it would be for an uncharged polymer of the same molecular weight in a good solvent. However it should be noted that this exponent differs somewhat from the relationship $R \sim Na$ discussed by de Gennes et al.[29] (N being the degree of polymerization), who considered the case where a, the monomer length, could be assumed to be comparable with the Bjerrum length. In this latter case, it follows from eq 13 that $C^* \sim 1/N^2$, whereas our result implies $C^* \sim 1/N^{1.3}$.

To consider how the mesh size ξ varies for the different solutions, the scaling ideas of de Gennes et al.[29] are again used. The first assumption of this model is that at the overlap concentration ξ is comparable with the radius of gyration R_g, and therefore

$$\xi_{C^*} = R_{C^*} = R_g \qquad (15)$$

Furthermore, as long as $C > C^*$, ξ must be independent of molecular weight. These two conditions lead to an equation of the form[29]

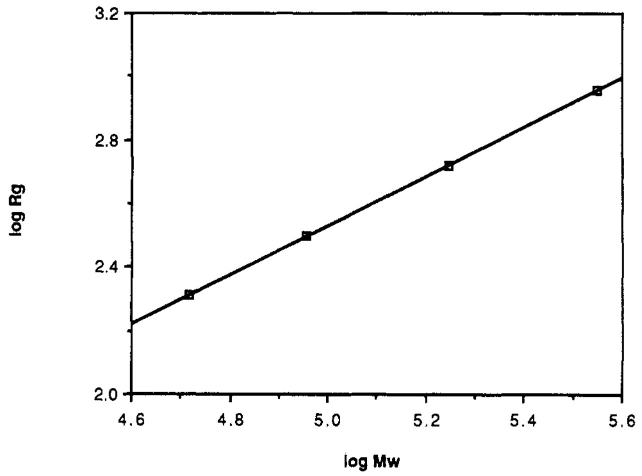

Figure 6. Plot of calculated R_g (Å) as a function of PLL M_w.

$$\xi = R_g(C^*/C)^{1/2} \qquad (16)$$

if R_g is taken to be linear in N. For the present case, the precise form for ξ will be slightly different, with an exponent of 0.6 to be consistent with the assumed relationship between R_g and C^*. However, it is not the precise form of this equation that is important. Rather, the point to note is that there is no molecular weight dependence of ξ.

Since at C^* ξ is comparable with R_g, it follows from the values given in Table I that for the two lower PLL molecular weights the radii of the probe particles used are always larger than ξ. For the two higher molecular weights at low PLL concentrations, the smaller of the two probe particles has a radius comparable with or even smaller than ξ; for the larger 800-Å-radius particles, the probe particle radius always exceeds ξ in all but the most dilute solutions of the highest molecular weight polymer. It follows, therefore, that most of the data presented below corresponds to the case of $R > \xi$. As will become apparent, however, there is nothing to indicate that the probe particle diffusion is in any way different above and below the point where $R/\xi = 1$.

Small-angle X-ray scattering[30] has been used to give an independent measure of the radius of gyration of the sample of 90 000 molecular weight at a concentration below C^* and of the correlation length above C^*. The measurement of R_g was difficult because of the extremely low signal intensity, making an accurate determination hard to achieve. A value of ~200 Å was obtained, somewhat lower than the value calculated from the intrinsic viscosity data, although comparable. At a concentration of 10 g/L (i.e., well above C^*), the correlation length was found to be about 100 Å. This value is in excellent agreement with the value (104 Å) deduced from eq 15, slightly less so if the modified exponent of 0.6 is used.

Turning now to consider in more detail the concentration dependence of the sedimentation coefficient, Figure 7 is a plot of ln (ln S_0/S) as a function of ln C/C^* for all PLL molecular weights. The data have been plotted in this form (i.e., in terms of C^*) in order to remove any polymer molecular weight dependence, as suggested by the scaling arguments presented above—beyond C^* the network properties will depend only on ξ. The plot shows that, except for the highest molecular weight PLL at the highest concentrations, the points can be fitted to a single straight line, indicating the validity of scaling ideas for this problem. The straight line so obtained fits a stretched

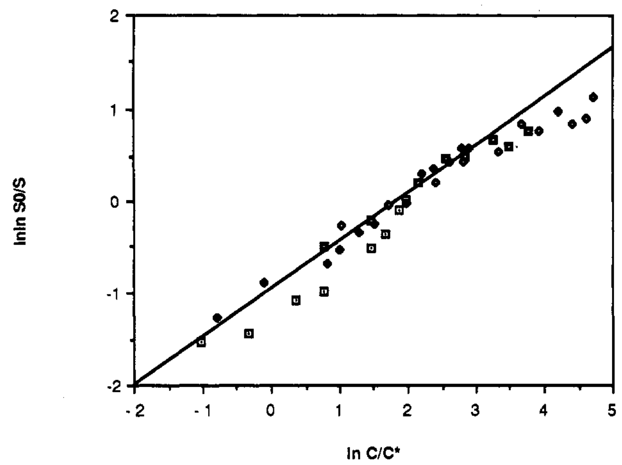

Figure 7. Plot of ln (ln S_0/S) as a function of ln C/C^* for PLL: (⊡) M_w 52000 g/mol; (◆) M_w 90000 g/mol; (□) M_w 175000 g/mol; (◇) M_w 353000 g/mol.

exponential form of the type given in eq 1 and 4. The values of ν and A determined from the line are found to be 0.51 and 0.33, respectively, agreeing well with Cukier's prediction of $\nu = {}^1/_2$ for the concentration dependence. At concentrations greater than about 50C^* for the highest molecular weight polymer, the points begin to deviate from the straight line, leading to a lower value for ν of 0.35 being determined for these solutions. This systematic deviation is thought to be due to entry into the regime where the solution has become concentrated rather than semidilute.

Discussion

As discussed in the Introduction, if ideal thermodynamic behavior occurs, and if the same frictional coefficient is operative in both sedimentation and diffusion, then measured D values and those calculated from sedimentation experiments should be in agreement. Figures 2 and 3 shows this comparison for the two probe sizes. For the larger particles, the two coefficients agree to within experimental error, but for the smaller particles some systematic difference is present, with the sedimentation data yielding higher values and more markedly so as the concentration increases.

Our experimental data can be compared with the work of Nemoto et al.[31] They used ultracentrifugation and PCS to study the sedimentation and diffusion of poly(methyl methacrylate) (PMMA, M_w = 343000) as the probe in thiophenol (TPH) solutions of polystyrene (PS) at different PS concentrations and molecular weights. They found agreement between D/D_0 and S/S_0 in solutions where $M_{PS} < M_{PMMA}$, but where the reverse was true, then D/D_0 was systematically lower than S/S_0 by about 30%. (In the present work, it would seem more probable that linear dimensions rather than equivalent molecular weights are the determining parameter, i.e., the relative magnitudes of R and ξ). It was suggested[31] that such discrepancies could be attributed to the relative magnitudes of the time scale of the experiment and the characteristic time for rearrangements of the PS network. For a PCS experiment, the time over which measurements are made is a few milliseconds and the distance of the order of micrometers, whereas in sedimentation, characteristic times and distances are of the order of a thousand times greater. In the context of Nemoto et al.'s experiments, it was argued that the time scale for network rearrangement in high molecular weight PS samples was similar to the time scale in the PCS measurement, leading to the existence of spatial correlations between the PMMA and PS molecules which could retard the PMMA diffusion. For low molecular weight PS, however, the network rearrangements were suggested to occur sufficiently rapidly that the situation approximates that pertaining to the sedimentation measurements, and therefore the two techniques agree. The present study supports the finding that where differences occur D/D_0 is lower than S/S_0.

Turning now to the stretched exponential expression for S/S_0 (eq 1), the results presented here can be compared with other results in the literature. Nemoto et al.[31] also fitted their data to a stretched exponential of the form $\exp(-AC^\nu)$ where the exponent ν was found to be 0.55 from diffusion and 0.67 from sedimentation for semidilute solutions of the highest molecular weight polystyrenes. Their ν agrees well with the value of 0.51 obtained here, despite the fact that the size of their probe was smaller than the average network mesh, whereas in this study the probes used were (in general) larger. However, whereas our data can be reduced to a universal curve of the form $S/S_0 = \exp[-A(C/C^*)^\nu]$, they reported that their data could not be so reduced.

In the present work, both probes are in general larger than the average mesh size of the transient polymer network. The curves shown in Figure 4 for S_0/S of the two probes have the same concentration dependence; in other words, there is no apparent difference in the way the two probes interact with the transient network. However, it is clearly desirable to extend the size range of probes studied in further work.

The pioneering work of Phillies et al.[3-10] has shown that the Stokes–Einstein equation need not in general be obeyed for probe particles in polymer solutions, and this finding has since been corroborated by other workers.[11,32-34] The extent of the deviation from Stokes–Einstein behavior seems to vary from system to system and is conveniently measured in terms of a parameter $k = R_{app}/R$. In this equation, R_{app} is the apparent radius, calculated from the Stokes–Einstein equation by using the macroscopically measured viscosity. For solutions of poly(acrylic acid) and PS spheres with sizes comparable to those used here, the ratio k was shown to become as small as 0.2 at pH ~8 (when the acid is dissociated) and in the absence of salt. The ratio was ~0.6 at the same pH but in the presence of 0.1 M NaCl.[10] Brown and Rymden[35] likewise demonstrated a value of k significantly less than unity for (hydroxypropyl)cellulose and (carboxymethyl)cellulose solutions, the latter exhibiting a less marked effect ($k \sim 0.6$ for the most concentrated solutions studied) than the former ($k \sim 0.35$). In a study of the uncharged polymer poly(ethylene oxide), Ullmann et al.[6] find that k can be greater than 1 for small particles, but this can be at least partly understood in terms of adsorption. For larger particles, k falls below 1 but with a complex concentration dependence.

Figure 8 shows a plot of $k = R_{app}/R_0$ as a function of PLL concentration, calculated from both sedimentation and diffusion data for the larger probe particles. For our data, k has been calculated noting

$$\frac{D}{D_0} = \frac{kT/(6\pi\eta R_{app})}{kT/(6\pi\eta_0 R_0)} = \frac{\eta_0 R_0}{\eta R_{app}}$$

and therefore

$$\frac{R_{app}}{R_0} = \frac{D_0\eta_0}{D\eta}$$

Here D_0 is the value measured during the determination of the adsorbed layer thickness at a much lower PLL concentration, in the plateau region of the adsorption isotherm. D has been taken as the value measured (for

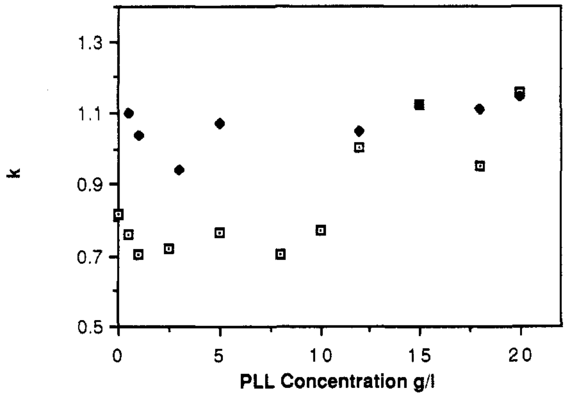

Figure 8. Plot of $k = R_{app}/R_0$ for PS probe of 800-Å radius as a function of PLL concentration: (⊡) k calculated from sedimentation data; (◆) k calculated from PCS data.

a given concentration) by PCS or calculated from sedimentation, to give the two different estimates of k. Because of the uncertainty in D_0 (and R_0) from the sedimentation data due to possibly density errors and charge effects as discussed above, the PCS data must be regarded as more reliable for this calculation.

Two points should be noted about Figure 8. Firstly, the deviations from Stokes–Einstein behavior (i.e., $k = 1$) are not as large as have been observed by some other workers. Secondly, and more importantly, the deviation is in the opposite sense (i.e., $k > 1$). This implies that the probe particle is diffusing more slowly than the bulk viscosity would predict, so that it appears to encounter a greater resistance than expected, even after accounting for the effect of PLL adsorption. (If the value for D_0 is taken as the value in the absence of any polymer at all, this is equivalent to ignoring the presence of the adsorbed layer. This leads to a significantly larger, but misleading, value for k.) As will be documented fully elsewhere, the hydrodynamic thickness of the adsorbed layer has been found to be 200 Å. The largest deviation from the Stokes law is seen at the higher polymer concentrations with k values (for the PCS data) of about 1.15. This deviation from unity lies outside the expected experimental error. As discussed above, in this context the sedimentation data are thought to be less reliable.

Thus, as Phillies has reported, the system does show a deviation from the Stokes–Einstein law. For probe particles that are smaller than the average correlation length of the mesh, this would perhaps not be very surprising, since the probe particles will be sensitive to some local microviscosity, as was discussed above. This study has concentrated, however, on probe particles larger than ξ, and at first sight these might be assumed to follow the Stokes relation, but do not. This result is consistent with other recent findings, which have shown[10] that even for micron-sized probe particles (i.e., $R \gg \xi$) the Stokes law is still not precisely obeyed, although the deviations are less marked than for smaller probe particles.

Phillies et al.[3,10] have suggested that one possible reason for the breakdown of the Stokes law could reside in the non-Newtonian nature of polymer solutions. To explore this point further, the sedimentation coefficient was determined over a range of rotational speeds. There was no variation in the measured sedimentation coefficient, within the limits of experimental accuracy. However, in doing this it is only possible to explore a fairly modest range of conditions, and this cannot be regarded as conclusive evidence against Phillies' argument.

Gorti and Ware[11] used fluorescence photobleaching recovery to measure the diffusion of fluorescein-tagged serum albumin and fluorescein-tagged polystyrene latex spheres through polystyrene sulfonate solutions, as a function of polymer concentrations and ionic strength. Phillies et al.[3-10] have explored a wide range of experimental configurations (in terms of the nature of the polymer, the size of the probe, and the effect of changing pH and/or ionic strength) via the technique of PCS. Both groups have fitted their data to eq 1, finding ν to range between 0.5 and 1.0 as a function of ionic strength. It has been suggested[32] that there is a systematic increase in the value of ν as the characteristic time for relaxation of the polymer network becomes sufficiently short that the network can no longer be treated as fixed, as implied in the theoretical model of Cukier.[14] Thus ν will tend to be higher for flexible or low molecular weight polymers. However, for polyelectrolyte solutions, the presence of charge effects is an additional complication. Thus Gorti and Ware[11] suggest that ν will be greatest (i.e., close to unity) under conditions of maximum intersegment interaction, corresponding to low-salt, high charge density, high molecular weight conditions. Nevertheless, in our system without salt, a value for ν of close to 0.5 is found. Phillies et al.[10] found a complicated set of dependencies on C, R, and pH. They advocated a nonunique model to describe their observations. At pH 7 and fixed C they found $\delta = 0$ in the absence of salt, in agreement with this study. Since the earlier work cited by Langevin and Rondelez, the experimental data reported in the literature have not supported the theoretical estimate of $\delta = 1$ seen in eq 4.

All experimental data reported above have shown that some deviation from Stoke's law is observed. It is first necessary to consider whether the observed effects could be attributed to slow and incomplete mixing, in which the polystyrene spheres remain in void spaces containing solvent but little polymer, while the polymer is present at high concentration in regions containing few spheres. Such spatial inhomogeneity could be created by insufficient stirring after adding the polystyrene latex spheres to the polymer solutions. However, for the system under study here, no difference was found between samples studied after only 2 h, 24 h, or more from their initial time of preparation, thus indicating that the results do correspond to a steady state.

We now turn to discuss the various theories discussed in the Introduction and embodied in eq 3 and 4. In deciding whether R is greater or less than ξ, it is implicitly assumed that ξ has a well-defined value. This must be regarded as a simple approximation, the mesh size in reality exhibiting some kind of distribution, with ξ as its mean. Although for many instances consideration of this mean value may be sufficient, it would seem that where $R \sim \xi$ the spread of pore size in the mesh will become important. It is then no longer possible to say that the probe is definitely bigger or smaller than the mesh size, because it is likely to be bigger than some pores but smaller than others.

In addition, only if the probe diffusion occurs on a time scale much greater than the cooperative diffusion of the polymer network does ξ acquire a physical significance. Otherwise, the (implicit) time averaging of the fluctuating mesh is meaningless. In general, quantities such as the root mean square fluctuation

$$\langle \delta\xi_t^2 \rangle^{1/2} = (\langle \xi_t^2 \rangle - \langle \xi \rangle^2)^{1/2}$$

will be more relevant.

That the semidilute regime must be considered to be inhomogeneous is supported by recent work reported by Brown et al.[32,33,36] They showed three discrete distributions present in their PCS data on the (monodisperse) PS/ethyl acetate system, which suggests the presence of inhomogeneity in this regime. It seems likely, therefore, that idealized homogeneous models assumed in the literature will be inadequate for describing the present and similar situations.

On the basis of this and other published work, the following picture emerges. The probe may be imagined to diffuse by passing through pores formed by entangled polymer segments. It will only go through when the size of the pore is greater than its radius R. The pore size fluctuates on a time scale determined by the cooperative diffusion of the polymer mesh. However, this is no longer relevant when the particle size is smaller than all the pores present in the solution. Thus, when $R \ll \xi$, the particle can diffuse within the mesh relatively unhindered, and much work on the diffusion of low molecular weight material through gels demonstrates this feature. At the other extreme, when R exceeds the largest pore size, then Stokes' law may again be applicable, providing adsorption effects are taken properly into account. In the intermediate range, where $R \sim \xi$, deviations from Stokes' law must be expected, and their extent will depend on the actual property measured, particularly its time and spatial scales.

Conclusion

We have observed probe diffusion and sedimentation in a polyelectrolyte solution, noting the dependence of D and S on major experimental variables: polymer concentration, molecular weight, probe radius, and solution viscosity. The data from diffusion and sedimentation experiments show some differences for small particles in concentrated PLL solutions. We have found a universal curve for the molecular weight dependence of D (or S) which is predicted by scaling theory. We have also found the concentration dependence to agree quite well with the Cukier prediction: ν was found to be 0.51 for all molecular weights studied, which agrees very well with the predicted exponent of 1/2. However, no dependence on probe radius is found, suggesting that the available theoretical predictions are not entirely satisfactory (although the range in R values used was small). The particle diffusion does not precisely obey the Stokes–Einstein law. Furthermore, there seems to be no substantial difference between the data reported here, for a system in which R is greater than or comparable with ξ, and other work reported in the liteirature, for which R is less than ξ. This may arise because a theory based upon a single value for the mesh size must be a gross approximation.

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