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A QELS–SEF Study on High Molecular Weight Poly(lysine): Field Strength Dependent Apparent Diffusion Coefficient and the Ordinary–Extraordinary Phase Transition

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ABSTRACT: We have used the quasi-elastic light scattering–sinusoidal electric field (QELS–SEF) technique to study the electric field strength (E) dependence of the apparent diffusion coefficient of poly(lysine) as computed from the line width of the frequency-shifted spectrum (D_{SF}). Spectra were obtained with a driving frequency of 90 Hz for $3 < E < 30$ V/cm in 0.5 and 10 mM KCl solvents, where D_{SF} was observed to increase as the value of E increased. In comparison with the apparent diffusion coefficient obtained by conventional QELS results (D_{app}), the low- and high-field extrapolation limits of D_{SF} are suggested to be equal to the values of D_{app} for this preparation of poly(lysine) in 0.5 and 100 mM KCl, respectively. The field strength dependence of D_{SF} is interpreted in terms of small-ion effects and the disruption of *temporal aggregates*.

Introduction

Quasi-elastic light scattering (QELS) studies on poly(lysine) solutions have revealed somewhat bizarre behavior of the apparent diffusion coefficient (D_{app}) as a function of added salt (C_s).[1-6] The value of D_{app} first rises as C_s is lowered and then drops catastrophically by over an order of magnitude for C_s concentrations below 10 mM. The region of C_s in which D_{app} increases has been referred to as the *ordinary phase*, whereas the region of C_s with anomalously low values of D_{app} has been referred to as the *extraordinary phase*.[1] The discontinuity therefore defines a critical salt concentration (C_c), whose value tends to increase with an increase in the poly(lysine) concentration (C_p). Concomitant with these QELS observations was the observation that the total intensity of scattered light monotonically decreased over the entire C_s range under investigation.[1,3,4] Martin et al.[7] suggested that the discontinuity in the C_s profile of D_{app} was a result of a disorder–order transition where the intensity of scattered light was suppressed through direct polyion–polyion interactions that maintained the poly(lysine) in a lattice-like array. In contrast, other physical properties of the poly(lysine) system in the low ionic strength regime do not exhibit such bizarre behavior. The relative viscosity,[7] apparent electrophoretic mobility,[3,8] and apparent conductivity[9] exhibit a monotonic increase in value through this transition region, where very small changes (~1%) occur at C_c in the viscosity and conductivity data. Zero and Ware[3] reported that the tracer diffusion coefficient (D_{Tr}) obtained by fluorescence photobleaching recovery (FPR) techniques only drops in value by a factor of 2 in going from the high- to zero-added salt conditions. The FPR data clearly indicate that the majority of the poly(lysine) molecules are not fixed in lattice arrays but are free to diffuse throughout the solution. There appears then to be a paradox between the QELS and FPR interpretations. The collective motions for poly(lysine) (D_{app} obtained from QELS data) appear to be extremely sensitive to the ionic strength of the solvent, whereas the motions of the individual molecules (D_{Tr} computed from the FPR data) appear to be oblivious to the ionic strength conditions of the solvent.

It is of interest to note that the apparent diffusion coefficients computed from the line width of the electrophoretic light scattering (ELS) data (D_{ELS}) are smaller than the values of D_{app} obtained for $C_s > C_c$, but larger by a factor of 2–10 than D_{app}[3,8] at the same added-salt conditions. The value of D_{app} for $C_s < C_c$ is much too small to be associated with the mutual diffusion coefficient for the poly(lysine) system. Likewise, the solutions are much too dilute to associate this slow decay mode with hindered diffusion which might occur in congested solutions. The tracer diffusion studies clearly eliminate these two possibilities. Since the origin of the anomalously slow mode for $C_s < C_c$ is not known, we prefer to label this decay process as *jeu de molécules somnolentes*, and reserve the notation D_{jms} for the apparent diffusion coefficient associated with this process.

There also appears to be some controversy as to whether two relaxation processes are present for $C_s > C_c$. In the initial studies on poly(lysine), only one relaxation time was reported on either side of C_c[1-3] although two relaxation times were reported at the critical concentration C_c.[1,6] In contrast to these low molecular weight preparations (<500 000 daltons), two relaxation times were evident in the correlation function for higher molecular weight preparations, provided data were taken at very low scattering angles.[4,5] In other systems where splitting of D_{app} into two domains was observed, such as for the mononucleosomal DNA (~140 base pairs)[10] and dinucleosomal DNA (~375 base pairs)[11] systems, two relaxation domains were discernible in the correlation function for a very broad ionic strength range. Likewise, the rate constant for the slow mode was only a factor of 3–4 smaller than that for the fast-decay mode over the ionic strength ranges reported. The precipitous drop in D_{app} below C_c for the poly(lysine) system was attributed to the possible role of nonlinear effects in the small-ion distribution, which might affect both the decay rate and the scattering power of the poly(lysine).[4,5] Recent data on poly(styrenesulfonate)[12] show behavior which parallels that of poly(lysine), so this unexpected behavior is not characteristic of the poly(lysine) molecule.

We report in this paper quasi-elastic light scattering experiments in which a sinusoidal electric field is applied across the sample (QELS–SEF). This technique was previously used to study DNA,[13,14] mononucleosomes,[14-16] and polynucleosomes[16] in low ionic strength buffers, where a dispersion relation in the apparent electrophoretic mobility[13-16] and line width[16] was observed as the driving frequency fell below 100 Hz. In view of the parallels in experimental design and observations of low-frequency dispersion effects of measured parameters for the QELS–SEF and dielectric relaxation techniques,[17-19] we have adopted the models used in the dielectric studies to interpret our data. Current opinion is that the dielectric relaxation dispersion is due to fluctuations in the small-ion concentration in the vicinity of the polyion.[17-22] We report in this paper the electric field strength dependence of D_{SF}

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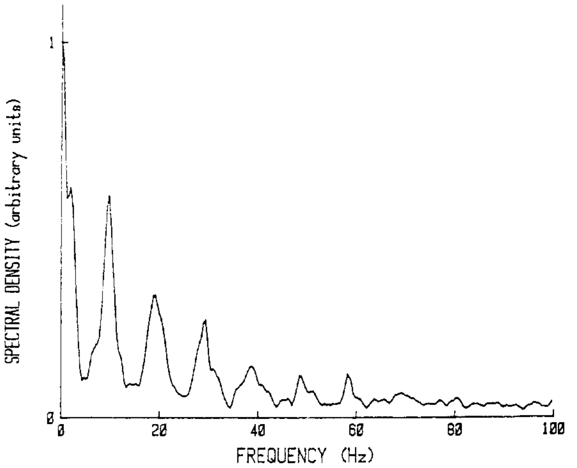

Figure 1. Spectral density of poly(lysine). The spectral density profile of poly(lysine) in the presence of a 10-Hz sinusoidal electric field is shown. In accordance with the theory outlined in the text, peaks are located at the driving frequency and harmonics and the relative amplitudes appear to obey the Poisson distribution. The scattering angle was 6°.

and compare these values with the high- and low-field limits to D_{app} obtained by conventional QELS methods.

Methods

Highly polymerized poly(lysine) was purchased from Sigma Chemical Co. (degree of polymerization 3800 with a reported viscosity-average molecular weight $M_\eta \sim 800000$). The poly(lysine) was first dissolved in doubly distilled water and then dialyzed against doubly distilled water made up to pH 7.4. Aliquots of this solution were then dialyzed against the appropriate KCl solutions, also at pH 7.4. The concentrations were determined from optical absorbance measurements using $A_{240} = 0.1$ for a 1 mg/mL solution.

The QELS-SEF facility has previously been described,[13-16] where we have employed platinized platinum parallel-plate electrodes with the following gap dimensions: height = 0.32 cm, length = 1.27 cm, and width = 0.32 cm. The voltage drop amplitude (V) of the applied sinusoidal field was monitored with a Tektronix oscilloscope, where the electric field amplitude (E) was computed from the relationship $E = V/d$.

A Spectra Physics Model 165-07 argon ion laser operating at a wavelength of 488 nm was employed in these studies, where the power was less than 100 mW. The heterodyne signal was obtained by splitting the incident beam with a beam splitter (50%), diverting the split portion of the beam by two mirrors to a pin at the observation side of the scattering cell, and then focusing the image of the pin on an observation window by means of a reflex mirror arrangement.[13-16] The relative intensity of the heterodyne beam was adjusted by placement of neutral-density filters between the two mirrors.

All data were taken at a scattering angle (θ) of 6° and the temperature of 20 °C. The temperature was maintained constant by circulation of water through the jacketed ELS cell.

Spectra were obtained with a Hewlett-Packard 3285A real-time spectrum analyzer (256 points), where 8–16 spectra were averaged for each run. The spectra were stored in a Hewlett-Packard 86A microcomputer. According to the current theory for the QELS–SEF experiment, the spectral density profile should contain peaks located at the driving frequency and its harmonics, where the relative amplitudes should follow a Poisson distribution.[13-16] This prediction is borne out in the spectrum illustrated in Figure 1 for a driving frequency of 10 Hz.

To avoid possible complications in analysis that might occur for overlapping peaks, data in this study were obtained with a driving frequency of 90 Hz. These spectra were then analyzed with a nonlinear least-squares program developed in our laboratory, where the spectral density profile $S(K,\omega,\omega_{\mathrm{d}})$ is of the assumed Lorentzian form

$$S(K,\omega,\omega_{\mathrm{d}}) = A/[H^2 + S^2] + B \tag{1}$$

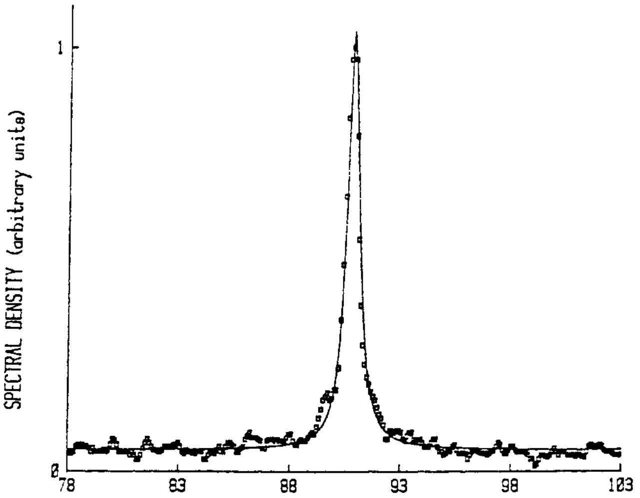

Figure 2. Frequency-shifted spectral density of poly(lysine) in 10 mM KCl. The applied voltage across the system when the above spectrum was taken was 3 V. The line width yielded an apparent diffusion coefficient of 0.064 ficks when fitted to a single Lorentzian function (solid curve).

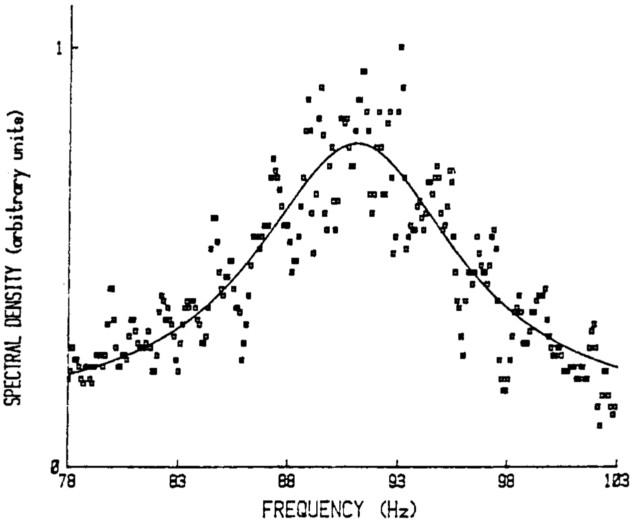

Figure 3. Frequency-shifted spectral density of poly(lysine) in 10 mM KCl. The above spectrum was obtained for an applied voltage of 10 V. A least-squares fit of a single Lorentzian function (solid line) resulted in an apparent diffusion coefficient of 1.097 ficks.

where A is a relative amplitude, B is the base line, and H is the half-width of the frequency-shifted peak located at the frequency S. The least-squares parameters are related to the molecular and experimental parameters by the expressions

$$H = D_{\mathrm{SF}}K^2/2\pi \tag{2}$$

$$S = (\omega - \omega_0 - \omega_{\mathrm{d}})/2\pi \tag{3}$$

where $K = (4\pi n/\lambda)\sin(\theta/2)$ is the scattering vector, D_{SF} is the effective diffusion coefficient for the sinusoidal field experiment, $\omega_{\mathrm{d}}/2\pi$ is the frequency of the applied field (90 Hz in these studies), and $\omega_0/2\pi$ is the frequency of the incident light.

Results

Representative spectral density profiles are shown in Figures 2 and 3 for poly(lysine) in 10 mM KCl solvent. Similar broadening of the line width with increasing field strength was observed for the 0.5 mM KCl solvent. The solid line in these figures is the nonlinear least-squares fit of a single Lorentzian function to the data. The values of D_{SF} computed from the least-squares line widths are presented in Table I for the various applied field strengths.

Table I
Comparison of QELS and QELS-SEF Results[a]

$D_{app}(N\Delta t=\infty)$	D_{SF}	[KCl], mM
1.16		100
0.035	0.048 (1)	10
	0.066 (2)	10
	0.38 (6)	10
	1.10 (10)	10
0.026	0.092 (2)	0.5
	0.095 (4)	0.5
	0.39 (8)	0.5
	0.35 (10)	0.5

[a] The asymptotic limits at infinite time were obtained from QELS data. The values of D_{SF} were obtained from a single Lorentzian fit to the data, where the values in the parentheses are the measured voltaged applied across the electrodes. (See text for details.) $C_p \sim 2.5$ mg/mL.

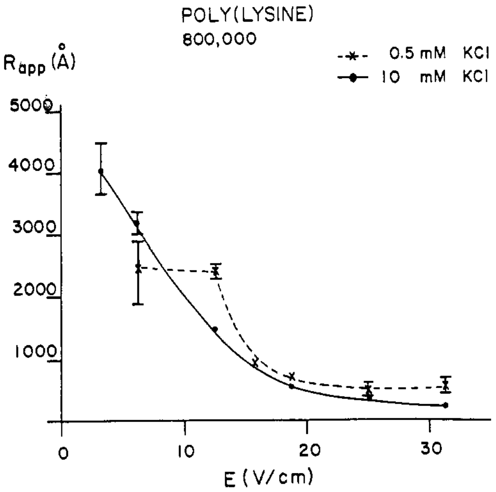

Figure 4. Apparent radius of poly(lysine) as a function of field strength. The apparent radius of poly(lysine) was computed from D_{SF} using the Stokes–Einstein relationship and plotted above as a function of the applied electric field. These data suggest R_{app} approaches asymptotic limits for the field strengths used in this study. Deviations from the above behavior is expected for higher fields.

The apparent radius (R_{app}) of poly(lysine) was computed from D_{SF} using the Stokes–Einstein relationship, $D_{SF} = kT/6\pi\eta R_{app}$, and plotted as a function of field magnitude E in Figure 4. We also summarize in Table I relevant results of our QELS study on the same preparation of poly(lysine),[5] where the data collection interval was sufficiently long that the 64-point correlation function decayed to the base line (indicated by the asymptotic limit $N\Delta t = \infty$, where N is the number of delay channels and Δt is the data collection interval). The value of D_{app} was obtained from a nonlinear least-squares fit of a single-exponential function to the correlation function.

There are two important characteristics of the spectra obtained in this study. First, the line width broadens as the electric field strength is increased. This suggests that the apparent radius of the poly(lysine) decreases as the field strength is increased. The second observation is that the quality of the frequency-shifted peak decreases with an increase in the electric field strength. There are at least two possible causes for the decrease in quality: the number of scattering units contributing to the intensity has decreased and/or the intrinsic scattering power of each unit decreased with an increase in the field strength.

Comparison of the extrapolated electric field limits of R_{app} suggested in Figure 4 with the values of the poly(lysine) radius computed from D_{app} given in Table I suggests the following equalities for D_{SF}, the latter being solely obtained under the condition $C_s < C_c$

$$D_{SF}(E > 25 \text{ V/cm}) = D_{app}(C_s \gg C_c) \quad \text{(high-salt limit)} \tag{4}$$

$$D_{SF}(E = 0) = D_{jms} \tag{5}$$

where it is again emphasized that $N\Delta t = \infty$ for the QELS data. It is to be emphasized that the inequality $E > 25$ V/cm is confined to the extrapolated limit *of data presented* and does not include nonlinear effects that will occur when higher field strengths are applied.

Discussion

There are two features of the poly(styrenesulfonate) and the poly(lysine) systems which appear to differ from other polyelectrolyte systems reported in the literature: (1) the highly cooperative nature of the splitting process as inferred from the rapid change in decay rates over a narrow ionic strength range and (2) the magnitude of the splitting between the fast and slow relaxation times, by greater than a factor of 10. It is our current belief that these two decay domains are manifestations of the same mechanism;[4,5,23-25] hence the understanding of one process should provide insight into the understanding of the other process. We first focus on the interpretation of the rates of these processes and then comment on the relative amplitudes.

There are two possible interpretations for the observed initial increase in D_{app} with a decrease in C_s (the ordinary phase). The most popular model involves direct repulsive interactions between the polyions, where the apparent diffusion coefficient is proportional to the reciprocal structure factor $S(K)$,[26,27] viz. the total intensity of scattered light

$$S(K) = 1 - (4\pi\rho/K)\int(g(r) - 1)r \sin (Kr)\,\mathrm{d}r \tag{6}$$

where ρ is the number density of the polyions and $g(r)$ is the distribution function, $g(r) = \exp(-U(r)/kT)$, where $U(r)$ is the pairwise interaction potential. In the limit $K = 0$ eq 6 reduces to that of the osmotic compressibility. If the screened coulomb potential is then employed for the pairwise interaction between polyions

$$U(r) = Z_p^2e^2 \exp(-[r - 2a_p]/\lambda_{DH})/r \tag{7}$$

where e is the magnitude of the electron charge, λ_{DH} is the Debye–Hückel screening length, Z_p is the polyion charge, and a_p is the hydrodynamic radius of the polyion, one obtains for the expression D_{app}

$$D_{app} \sim D_{Tr}(1 + Z^2C_p/2C_s) \tag{8}$$

where D_{Tr} is the high-salt value of D_{app}, assumed to be equal to the tracer diffusion coefficient. This expression also obtains for small ion–polyion coupled mode theories.[1,28] *It is therefore not possible to distinguish between direct polyion–polyion interaction models and small ion–polyion coupled mode theories on the basis of light scattering data alone!* We therefore focus on the possible interpretations of the QELS–SEF results and correlate these data with the other physical measurements on poly(lysine).

The relationships expressed in eq 4 and 5 suggest that the mechanism responsible for the jms process is disrupted when the field strength is increased. Implicit in eq 4 is that the mechanism responsible for the increase in D_{app} with decreasing salt for $C_s > C_c$ is also disrupted when the field strength is increased. This conclusion is based on the observation that the high-field limit of D_{SF} is approximately equal D_{app}(high salt) rather than the value of D_{app}

anticipated from coupled mode theories. This observation is consistent with the recent theoretical results of Fixman and Jagannathan,[29] who examined the effect of electric field strength on the ion cloud about an isolated polyion. One conclusion of their study is that moderate electric fields tend to strip off part of the ion atmosphere. We previously suggested that small ions were responsible for both the fast mode, in accordance with current theories,[1,28] and the jms mode, which resulted from the sharing of small ions as the ion cloud of neighboring polyions overlapped;[4,5,24] then the presence of an electric field of moderate strength might therefore disrupt all coupling between the various components. If this were the case then the equality expressed by eq 5 would result.

Unbeknownst to us at the time we proposed our model, Fulton had earlier proposed a conceptually similar model for the interpretation of dielectric relaxation data, but with a more firm theoretical foundation for the particular problem under examination.[30-33] Where we had localized fluctuations in the small-ion distribution to the physical exchange of small ions between overlapping ion clouds about the polyions, Fulton examined phenomenological transport expressions for the relaxation of charge transport. The time required for a disturbance in the charge distribution in a conducting medium to relax to equilibrium is given by the Maxwell relaxation time $\tau_M = \epsilon_e/4\pi\sigma$, where ϵ_e is the zero-frequency dielectric constant of the medium and σ is the zero-frequency value of the total conductivity of the solution. The value of τ_M clearly increases as the ionic strength of the medium is decreased; hence long-range correlations between fluctuating dipoles persist over longer periods of time. This result is conceptually equivalent to the decay of temporal aggregates, as postulated for the interpretation of the jms mode in the QELS correlation functions.[4,5,23-25]

The observation that the line width of the QELS-SEF spectra, and hence D_{SF}, increases with electric field strength and the suggestion of the limiting values of D_{SF} given by eq 4 and 5 appear to be consistent with the small ion-polyion coupled mode model. We now address the quality of the data as a function of electric field strength in terms of small-ion interference effects on the intrinsic scattering power of the polyions.

The system composed of polyions and small ions is a three-component system: the solvent (water), the thermodynamically free small ions, and the polyion-associated small ion complex. If the latter component is considered to be the scattering unit, then the scattering power of the unit is decreased relative to the neutral polymer because of interference effects of the associated small-ion cloud.[34-37] The criterion for interference is that there must be a deficit of co-ions, a condition which results when the linear solution to the Poisson-Boltzmann equation is not valid. We approximate the conditions necessary to give a deficit of co-ions, or equivalently an excess of small ions about the polyion, by the expression

$$C_{\text{excess}}/C_0 = [\exp(-U(r)/\epsilon kT) + \exp(+U(r)/\epsilon kT) - 2]/2 \quad (9)$$

where C_{excess} is the excess concentration of small ions relative to the bulk concentration C_0, ϵ is the dielectric constant of water, and $U(r)$ is a screened coulomb potential similar to that defined by eq 7 except Z_p appears to only the first power (the small ions are assumed to have unit charge) and the exponential argument is replaced by $(r - a_p)/\lambda_{DH}$. We have tailored the calculations to the present poly(lysine) system: $Z_p = 3800$ (degree of polymerization) and $a_p = 180$ Å. The ratio C_{excess}/C_0 is plotted as a function of the Debye-Hückel screening length (λ_{DH}) and radial distance (r) in Figure 5. These calculations suggest that a large excess of small ions begins to appear in the vicinity of the polyion for $C_s \sim C_c$. It should be mentioned that recent Monte Carlo calculations of Le Bret and Zimm[38] for the small-ion distribution about a cylinder suggests an enormous difference (by 3 orders of magnitude) in concentration about the cylinder as compared to the bulk solution. It might be inferred, therefore, that the intrinsic scattering power of the *isolated* poly(lysine) molecules can be drastically reduced if there exists a shell of small ions about the polyion. The relative scattering power of the *temporal aggregate*, assumed responsible for the jms mode, would be larger than that of the isolated polyion for at least two reasons: the larger number of polyions associated with the scattering unit, and delocalization of the small ions shared by the polyions, which would result in an increase in the intrinsic scattering power of each polyion. An increase in the applied electric field would decrease the total intensity of scattered light since the *temporal aggregates* would be disrupted, a prediction which is consistent with the spectra presented in Figures 2 and 3.

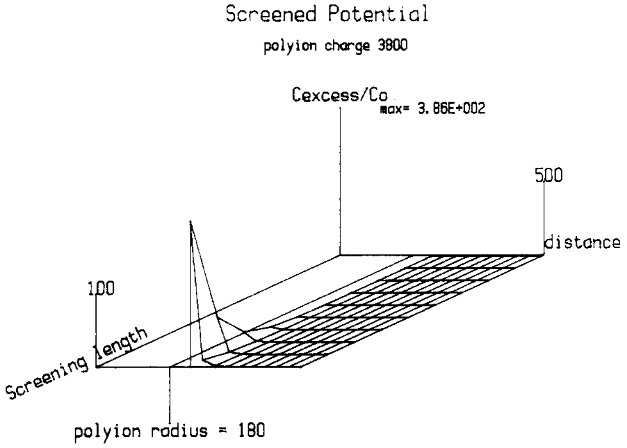

Figure 5. Excess small-ion concentration about poly(lysine). The relative excess concentration of small ions about a polyion (C_{excess}/C_0) was computed from eq 9 using a screened coulomb potential. The parameters employed were those for poly(lysine) used in the QELS-SEF studies: $Z_p = 3800$ (degree of polymerization) and $a_p = 180$ Å (computed from the high-salt value of D_{app}). The distance of closest approach to the polyion surface in these calculations was 25 Å. The Debye-Hückle screening length (λ_{DH}) was an adjustable parameter and related to the ionic strength by eq 12. As indicated above, there is a very large excess of small ions about the polyion around $\lambda_{DH} \sim 100$ Å, or $C_s \sim 0.001$ M.

Recent small-angle X-ray scattering data of Kaji et al.[39] on the poly(vinyl hydrogen sulfate) (PVHS) support the hypothesis that small ions are important in determining the scattering properties of the polyions. These authors showed that the intensity of scattered X-rays by a solution of PVHS exhibited a single peak as a function of scattering angle and that the peak position and intensity depended on the cation present (Li^+, Na^+, or K^+). They concluded that the small ions were localized, i.e. condensed, in the vicinity of PVHS. As also pointed out by these authors, the occurrence of a single maximum in the angle profile of the total intensity suggests only that pair correlations are important and does not provide sufficient evidence of a long-range lattice array. These authors further point out that the absence of a peak located at about half of the intersegmental distance rules out the presence of a high concentration of small ions between the polyions, a mechanism proposed by Ise and co-workers[40,41] in suggesting isolated domains of lattice-like and dilute solution-like structures in polyelectrolyte systems. In view of the above discussion regarding small ion–polyion coupling, the question now arises as to what species in solution are involved in the pair correlation interpretation: polyion–polyion or polyion–small ion shell.

The importance of small-ion effects on the critical concentration C_c has also been underlined in the empirical expressions of Drifford and Dalbiez[13] and also Nemoto et al.[6] Drifford and Dalbiez[13] deduced the following criterion at $C_s = C_c$

$$(C_p b)/[(\sum C_i Z_i^2)Q] = Z_s \tag{10}$$

where b is the average contour distance between two successive charges on the polyion, Q is the Bjerrum length ($Q = e^2/\epsilon kT$, in cgs units, where ϵ is the relative permittivity of the solvent), and Z_s is the charge on the counterion. This expression was obtained from both the poly(styrenesulfonate) and poly(lysine) data. Nemoto et al.[6] obtained a qualitatively different result relating the critical polyion and salt concentrations from their poly(lysine) data

$$C_p^* = \text{constant} \times C_s^{*-0.53} \tag{11}$$

where the asterisk indicates the concentrations where the bimodal behavior occurs. It is of interest to note that these two empirical expressions predict opposite qualitative behavior for the transition region. According to eq 10, the value C_c increases with polyion concentration whereas eq 11 predicts C_c decreases with polyion concentration. We can offer no reason for the qualitative difference between these two results but add that our own data tend to support eq 10.

In order to provide some physical explanation for eq 10, we choose to rewrite this expression in terms of the Debye–Hückel screening parameter λ_{DH}

$$(1/\lambda_{DH})^2 = 8\pi Ne^2 I_s/1000\epsilon kT = 8\pi N I_s Q/1000 \tag{12}$$

where I_s is the ionic strength due to the added salt ($I_s = (1/2)\sum C_i Z_i^2$) and N is Avogadro's number. Upon substitution of eq 12 into eq 10 and rearrangement, one obtains

$$(4\pi C_p N/1000)(b/\lambda_{DH}^2 Z_s) = 1 \tag{13}$$

The quantity $4\pi C_p N/1000$ is equal to $3/V_p$, where V_p is the volume per monomer unit of the polymer. The quantity $b/\lambda_{DH}^2 Z_s$ can be interpreted as the available Debye–Hückel volume along the polyion axis per unit charge of the small ion, and denoted by V_{DH}, where the cylinder height is b and the radius is $1/\lambda_{DH}$. Equation 12 can therefore be expressed in terms of these volumes

$$V_{DH} = V_p/3 \tag{14}$$

Couched in this form of volume ratios, the empirical expression of Drifford and Dalbiez[12] suggests C_c occurs when the small-ion atmospheres of neighboring polyions begin to overlap since the inequality $V_{DH}/V_p > 1$ obtains for $C_s < C_c$. The empirical expression of Drifford and Dalbiez tends therefore to support our hypothesis that the jms mode reflects the decay of temporal aggregates which are stabilized by the fluctuation forces arising from the sharing of small ions in the overlapping ion atmospheres.

Conclusions

The dynamics of poly(lysine) in low ionic strength solvents was examined by QELS–SEF techniques, where the effective diffusion coefficient D_{SF} was observed to increase with electric field strength. Since the QELS–SEF technique is the optical analogue to dielectric relaxation methods, this behavior is interpreted in terms of small-ion fluctuations that moderate long-range correlated motions between the polyions. As the field strength is increased, the more loosely bound small ions are stripped off the associated ion clouds, thereby disrupting these correlated motions.

It has also been suggested that nonlinear Poisson–Boltzmann effects of the small-ion distribution about the polyion lead to a decrease in the intrinsic scattering power of the *isolated* polyion. The highly cooperative nature of this phenomenon near C_c suggests that the so-called ordinary–extraordinary phase transition might be a result of a rapid change in relative amplitudes of the scattering from *isolated polyions* and the *temporal aggregates*. This interpretation is indirectly supported by lack of strong evidence by other physical techniques that a *true* phase occurs below C_c.

The suggestion that the jms mode results from overlapping ion clouds of neighboring polyions finds support in the empirical expression of Drifford and Dalbiez, where a relationship between C_p and C_s at the *transition point* was proposed. Rearrangement of their expression in the form of a ratio of volumes, the Debye–Hückel volume available per small-ion charge and the volume of monomer units, suggests that the transition occurs when this ratio approaches 1/3.

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Remarks on the Translational Diffusion Coefficient of Relatively Short Chains

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ABSTRACT: The expansion of the hydrodynamic radius R_H in inverse powers of $N^{1/2}$ is presented for three chain models which allow only for local structure along the chain. The effect of chain stiffness is included in one of the models. Formulas are presented to interpret R_H data for relatively short chains. The approach to the Gaussian chain limit as $N \to \infty$ is discussed.

Introduction

The discrepancy between the experimental value of the translational diffusion coefficient of a polymer molecule in a dilute solution, measured by quasi-elastic light scattering, and its theoretical value obtained from Kirkwood's approximate formula has revived interest in the theoretical calculation of the diffusion coefficient of macromolecules in solution. The discrepancy, first pointed out by Schmidt and Burchard,[1] refers to the observation that the measured value of the diffusion coefficient of a polymer at the Θ point, D, is about 15% smaller than the theoretical value D_0 calculated with the Kirkwood formula[2] for Gaussian chains, i.e., $D_0 = 0.1955 k_B T / b N^{1/2}$ with the usual meaning of the symbols. The magnitude of the approximation in this formula had been discussed earlier in the case of flexible chains with the preaveraged Oseen tensor. By obtaining the exact asymptotic solution of the Kirkwood–Risemann integral equation, Kurata and Yamakawa[3] calculated the diffusion coefficient as $0.192 k_B T / b N^{1/2}$. Zimm[4] showed that the Kirkwood formulation represents the diffusion coefficient of the center of resistance, and obtained $k_B T \nu_0 / \xi$ for the diffusion coefficient where ν_0 is the lowest Zimm eigenvalue and ξ is the friction coefficient per bead. He gave the numerical constant also as 0.192 instead of 0.1955. Horta and Fixman[5] obtained estimates for the magnitude of the correction to the Kirkwood formulas of about 1.68% of D_0, much smaller than the observed discrepancy. Recently, Zimm[6] obtained an upper bound for D_1/D, where $D_1 = D_0 - D$, in the case of the nonpreaveraged Oseen tensor as approximately 15%. Fixman[7] estimated D_1/D as about 8%, which is again not quite sufficient to explain the observed discrepancy mentioned above.

The physical nature of the approximation involved in the Kirkwood formula has been clarified essentially by Dubois-Violette and de Gennes[8] in 1968, for the case of the preaveraged Oseen tensor. They showed that D_0 is the short-time diffusion coefficient for the diffusion of the center of mass and does not take into account the coupling between the internal and translational motions. They also showed that the diffusion coefficient $D(t)$, defined in terms of the mean-square displacement of the center of mass as $\langle |\Delta R_c(t)|^2 \rangle = 6D(t)t$, varies gradually from D_0 to D as $t \to \infty$, due to deformation of the molecule during diffusion (see also Mansfield[9]). Using linear response theory Akcasu[10] derived a formal expression for $D(t) = D_0 - D_1(t)$ in the case of the nonpreaveraged Oseen tensor and calculated D_1/D_0 as a function of molecular weight when the Oseen tensor is preaveraged. The asymptotic analytical form of $D_1 = D_1(\infty)$ was first obtained by Fixman[7] in the case of nonpreaveraged hydrodynamic interaction.

The remaining discrepancy, of the order of 7–8% after the D_1 correction has been made, may seem to be too small to be of any physical significance. Since the accuracy of the measurement of the diffusion coefficient by light scattering is considered to be better than about 5%, and the measured value is consistently smaller than the calculated value, the remaining discrepancy has continued intriguing the theoreticians. Guttman et al.[11] calculated D_0 for chains created by Monte Carlo simulation in which both excluded volume and nearest-neighbor interactions are included, and found that the ratio $\rho = R_G/R_H$, where R_G is the radius of gyration and R_H is the hydrodynamic radius for such chains, is closer to the experimentally obtained ρ and differs from that obtained for an analytical Gaussian chain. In this and in a recent paper,[12] they also discussed the difficulties in extrapolating $1/R_H$ to its long-chain limit from the data obtained experimentally or by computer simulation. The question of extrapolation of the Monte Carlo results for short chains to long-chain limit has also been discussed by Fixman and Mansfield[13] recently.

The molecular weights used in the measurement of the diffusion coefficient by dynamic light scattering are usually less than 10^6 to satisfy the Guinier condition. The number of statistical segments N in such molecules may not be large enough for the long-chain Gaussian chain models to be applicable to the interpretation of the diffusion experiments especially if one worries about discrepancies of the order of 10% or less. The inverse moments of the

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