Macromolecules **1984**, *17*, 2376–2380

Dynamic Light Scattering Measurements of Diffusion in Polymer–Polymer–Solvent Systems

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Received January 31, 1984

ABSTRACT: Results of dynamic light scattering experiments on ternary (polymer–polymer–solvent) solutions are presented. Two distinct modes of decay are observed in autocorrelation functions of the scattered light. These are identified with the two independent modes of decay of concentration fluctuations in ternary solutions discussed by Pusey, Fijnaut, and Vrij for their recent theoretical work. The reasonable agreement between estimates of ternary diffusion coefficients based on irreversible thermodynamics and the dynamic light scattering results leads to the conclusion that for the particular combinations of concentrations studied here the diffusion coefficient of the fast mode corresponds to the mutual diffusion coefficient of the lower molecular weight polymer and the diffusion coefficient of the slow mode corresponds to the intradiffusion (or self-diffusion) coefficient of the higher molecular weight polymer.

Introduction

In a dynamic light scattering (DLS) experiment, the autocorrelation function of the intensity of scattered light may be measured, thus providing information about the time-dependent behavior of the scattering system.[1,2] When applied to polymer solutions DLS is, under certain conditions, capable of yielding measurements of the diffusion coefficient of the polymer. In the limit of infinite dilution the free particle diffusion coefficient D_0 is obtained.[2] At nonzero polymer concentrations the mutual diffusion coefficient D_m (present in Fick's law) measured by DLS has been shown to agree well with that obtained by conventional boundary relaxation measurements for solutions of dextran (a flexible polysaccharide) in water up to polymer concentrations of 200 kg m^{-3} over the molecular weight range 10 000–150 000.[3]

The dynamics of colloidal spheres has also been examined using DLS.[4] In recent work[5,6] it has been shown that for colloidal spheres with a small degree of polydispersity, two distinct modes of relaxation contributed to the autocorrelation function of scattered light for volume fractions of spheres greater than about 0.15. The two modes of relaxation were originally attributed to mutual diffusion and tracer or self-diffusion by Weissman.[7] A rigorous treatment of DLS from polydisperse systems including dispersions with bimodal size distributions has been given in Pusey et al.[8]

Experiments reported by Amis et al.[21-23] have shown that two modes of relaxation also exist in the autocorrelation function of light scattered from binary polymer solutions at intermediate concentrations. These two modes were shown to correspond to mutual- and self-diffusion processes. This interpretation is consistent with the work of Pusey et al. In addition, the results of DLS experiments on ternary polymer solutions in which one of the polymeric solutes has its refractive index matched by the solvent have been published by Lodge.[24] These experiments may also be interpreted by using the formalism of Pusey et al.

In this paper we investigate the use of the DLS technique to study aqueous ternary solutions containing two different polymers. The theoretical results of Pusey et al.[8] for DLS from dispersions of rigid, impenetrable particles are used in this paper to interpret experimental results, and a comparison is made between these results and those calculated using relationships derived from irreversible thermodynamics.

The experimental system chosen for this study consisted of a low concentration of a dextran polymer of intermediate molecular weight in a more concentrated solution of a lower molecular weight dextran. The concentration of the lower molecular weight component was varied. With the particular choices of concentrations and molecular weights used here, the intensity scattered by both components was approximately the same.

These experiments were performed with the aim of providing information about diffusion processes leading to structured flows in ternary polymer solutions.[9]

Theory

In this section, the results of Pusey et al. are first reviewed to show which quantities would be measured in a DLS experiment on a mixture of rigid, impenetrable particles, and the use of this treatment in describing DLS experiments on ternary polymer solutions is then discussed.

Provided that there is no appreciable volume change on mixing, the decay of spontaneous fluctuations in the concentration of two solutes (components 1 and 2) in a solvent (component 3) can be described by the following equations:

$$\frac{\partial}{\partial t}\delta c_1 = D_{11}\nabla^2\delta c_1 + D_{12}\nabla^2\delta c_2 \qquad (1)$$
$$\frac{\partial}{\partial t}\delta c_2 = D_{21}\nabla^2\delta c_1 + D_{22}\nabla^2\delta c_2$$

Here δc_i is a fluctuation from the mean molar concentration (mol m^{-3}) of component i and D_{ij} are diffusion coefficients.

If two new concentration variables are formed from linear combinations of c_1 and c_2, i.e.

$$\delta c_+ = \alpha_+\delta c_1 + \delta c_2 \qquad (2)$$
$$\delta c_- = \alpha_-\delta c_1 + \delta c_2$$

with

$$\alpha_\pm = \frac{(D_{11} - D_{22}) \pm [(D_{11} - D_{22})^2 + 4D_{12}D_{21}]^{1/2}}{2D_{12}} \qquad (3)$$

then eq 1 can be rewritten in a diagonalized form:

$$\frac{\partial}{\partial t}\delta c_+ = D_+\nabla^2\delta c_+ \qquad (4)$$
$$\frac{\partial}{\partial t}\delta c_- = D_-\nabla^2\delta c_-$$

Here

$$D_\pm = \tfrac{1}{2}(D_{11} + D_{22}) \pm \tfrac{1}{2}[(D_{11} - D_{22})^2 + 4D_{12}D_{21}]^{1/2} \qquad (5)$$

The diffusion equations (4) can be thought of as describing the decay of fluctuations in the total molar concentration ($\delta c_1 + \delta c_2$) at constant relative molar concentrations ($\delta(c_1/c_2) = 0$) for the + mode and fluctuations in the relative molar concentration at constant total molar concentrations for the − mode. They can be visualized as a total number density flucutation mode and a species exchange mode, respectively.[8] This description of diffusion processes in a system containing two solutes and a solvent is quite general and can be applied to systems containing either particulate or polymeric solutes. The only assumption is that irreversible thermodynamics can be applied. Note that the diffusion coefficients D_{ij} in eq 1 are defined in terms of molar diffusion fluxes (mol m^{-2} s^{-1}) relative to the mean volume velocity (which is zero here) with concentrations in units of mol m^{-3}. The D_{ij} have units of m^2 s^{-1} (see e.g., ref 10). If the equations in (1) are rewritten to involve diffusion coefficients defined in terms of mass diffusion fluxes and mass concentrations $C_i = M_i c_i$ the new diffusion coefficients D_{ij}' would be related to the D_{ij} through

$$D_{ij} = \frac{M_j}{M_i} D_{ij}' \qquad (6)$$

where M_i is the molar mass of species i (kg mol^{-1}).

In a DLS experiment, the spatial scale probed in a given measurement is determined by the magnitude of the scattering vector q, which is given by

$$q = \frac{4\pi n}{\lambda} \sin \frac{\theta}{2} \qquad (7)$$

Here, θ is the angle between the transmitted beam and the detector, λ is the wavelength of the incident light in a vacuum, and n is the refractive index of the scattering medium.

For dispersions of interacting spheres, the static structure factor, $S(q)$, which measures spatial correlations between particles, is strongly oscillatory and its main peak occurs at a given value of q, $q_{\max}$, which depends on the particles' sizes and interactions.[11] At values of q below $q_{\max}$ such that $S(q)$ is close to its zero q value, macroscopic thermodynamic properties are measured by time-averaged light scattering. Similarly, macroscopic dynamic properties such as the mutual and, for systems exhibiting scattering power polydispersity, tracer diffusion coefficients are measured by DLS in this q regime.

Pusey et al.[8] found that for dispersions containing two different sized species of rigid, impenetrable particles, DLS measurements made in the small q limit (i.e., $q/q_{\max} \ll 1$) would give a field autocorrelation function $g^{(1)}(\tau)$ of the form

$$g^{(1)}(\tau) = A_+ \exp(-D_+ q^2 \tau) + A_- \exp(-D_- q^2 \tau) \qquad (8)$$

In eq 8, τ is the delay time, D_+ and D_- appear in eq 5, and A_+ and A_- are the amplitudes of the number density fluctuation and species exchange modes, respectively. Calculations of A_+ and A_- were made by Pusey et al.[8] for the case of two solutes with hard-sphere interactions using the Percus–Yevick approximation.

Equation 8 can be expected to apply to DLS from any solute–solute–solvent system in which the two solutes are much more massive than the solvent and macroscopic diffusion is the only process contributing to the decay of the autocorrelation function of scattered light.

It is not immediately clear that eq 8 should be valid for a ternary polymer solution. The following arguments are given to justify its use in this work.

For binary polymer solutions at low concentration, the polymer molecules can be considered to behave as discrete particles. Hard-sphere models have been successfully used to describe the concentration dependence of the mutual diffusion coefficient D_m of polymers in good solvents at low concentrations.[12,13] This approximation is expected to be valid as long as intermolecular interpenetrations are not significant.

Because polymer molecules have a coiled structure, their ability to deform makes their dynamic behavior more complicated than that of spheres. In dilute solutions, these complications can be ignored when a suitable choice of the q vector is made. At sufficiently low values of q, such that $qR_G \leq 1$ (where R_G is the radius of gyration of a polymer molecule), the spatial scale probed by DLS measurements will be larger than the size of a polymer molecule and no internal motions will be observed. Translational motion of the centers of mass of polymer molecules (i.e., diffusion) will then be the only dynamic process contributing to the autocorrelation function of scattered light.[2]

At higher concentrations, where molecular overlap must inevitably occur, dynamic processs other than center-of-mass diffusion of polymer molecules may contribute to the autocorrelation function of scattered light.[14] Despite the increased nonexponentiality[14,16] of correlation functions measured for polymer solutions at intermediate concentrations, values of the apparent mutual diffusion coefficient extracted from the decay rate of correlation functions (both by the cumulant fitting[3,14,16] and single exponential fit[15] methods) agree well with boundary relaxation measurements of D_m. This requires further investigation because the causes of the nonexponentiality and its effects on the values of D_m extracted from correlation functions are not yet fully understood.

For the purposes of this work, it is sufficient to roughly estimate the concentration, C^*, required for the onset of overlap and it will be assumed that for concentrations below C^* no dynamic processes other than translational diffusion contribute to correlation functions measured at values of q such that $qR_G \leq 1$. A commonly used method of estimating the overlap concentration is to calculate the concentration of polymer required to give an overall concentration equal to that which would be found inside a single molecule if it occupied a volume R_G^3. In other words, it is a calculation of the concentration required for complete space filling by molecules occupying cubes of side length R_G. The resultant concentration, C^*, is given by

$$C^* = M/N_A R_G^3 \qquad (9)$$

where N_A is Avogadro's number.

A slight modification of this equation can be used to find the concentration C_1^* of one solute required for the filling of available space in the presence of a concentration C_2 ($C_2 < M_2/N_A R_2^3$) of another macromolecular solute

$$C_1^* = \left(1 - \frac{C_2 N_A}{M_2} R_2^3\right) \frac{M_1}{N_A R_1^3} \qquad (10)$$

The use of C_1^* here is only to estimate the overlap concentration and in no way does it assume any other significance. For the systems studied in this work, the concentrations are always below C_1^*, which confirms the validity of eq 8 for these polymer solutions.

Experimental Section

A. Materials. Dextran T20 (lot no. 5351), dextran T500 (lot no. 4094), and Sephacryl S-400 (lot no. GB 19006) were obtained from Pharmacia Fine Chemicals (Uppsala, Sweden). Sodium

Table I
Properties of Dextrans

dextran type	M_w/kg mol^{-1}	M_w/M_n	$D_0/10^{-11}$ m^2 s^{-1} (25 °C)	R_G[b]/nm
T20[a]	20.4	1.24	7.54	4.83
F600	864[c]	1.3[d]	1.08[d]	34.1

[a] See ref 3. [b] Calculated using $R_H = 0.665R_G$, where R_H is the hydrodynamic radius of the polymer molecule. (Although strictly only valid for nondraining linear Gaussian chains, this equation describes dextrans well.[3] [c] From time-averaged light scattering. [d] From DLS.[17]

chloride (analytical reagent) came from May and Baker Australia Pty. Ltd.

B. Sample Preparation. Dextran T500 dissolved in 0.1 M NaCl was fractionated on a Sephacryl S-400 column (dimensions 72.5 × 5 cm), and the fractions were monitored by optical rotation. Fractions corresponding to K_{av} values between 0.05 and 0.16 were collected and pooled after 15 column runs. The pooled sample was then concentrated by ultrafiltration and stored at 4 °C. This material is designated Dextran F600. Some of the properties at dextran T20 and dextran F600 are given in Table I.

Solutions with dextran F600 concentrations (C_2) of approximatly 5 kg mg^{-3} and dextran T20 concentrations in the range 40 kg m^{-3} $\leq C_1 \leq$ 170 kg m^{-3} were made in 0.1 M NaCl using double-distilled water as described previously.[3] All solutions were autoclaved for 10 min before use.

Use of eq 10 with C_2 = 5 kg m^{-3} shows that $C_1{}^*$ = 225 kg m^{-3} which is greater than the concentrations used here.

Dynamic light scattering measurements were performed on filtered samples[3] at 25.0 ± 0.1 °C. The light source was a Spectra Physics argon ion laser operating at λ 488 nm. The scattered light was detected with an EMI D260B photomultiplier tube in a Precision Devices (Malvern) RR109 photomultiplier assembly, and intensity autocorrelation functions were computed using a 96-channel Precision Devices (Malvern) digital correlator (Model K7023) operating in the single scaling mode.[1] Data acquisition times were always long enough for the last few points of the unnormalized correlation functions to reach at least 10^6 counts.

Normalized intensity autocorrelation functions $C(\tau)$ were converted to estimates of the field autocorrelation function $y_i(\tau)$ using the Siegert relation.[1]

$$y_i(\tau) = (C(\tau) - 1)^{1/2} \tag{11}$$

Experimental data were analyzed by fitting $y_i(\tau)$ with a sum of two exponentials and then using the parameters obtained as starting values for another fit which included a base line in the model for $y_i(\tau)$.

Thus the model which was used to fit $y_i(\tau)$ took the form

$$y_i(\tau) = \gamma[A \exp(-D_+q^2\tau) + (1 - A) \exp(-D_-q^2\tau)] + \Delta \tag{12}$$

where γ, A, D_+, D_- and Δ are free parameters determined by the fit, Δ being the optional base line.

In some cases data sets were constructed from correlation functions measured at two sample times usually a factor of 10 different from each other. Measurements of correlation functions were reproducible to within random errors and several correlation functions were often averaged to improve the statistical reliability of the results. When correlation functions were averaged, the equivalent data acquisition time was large enough for the last few channels to contain about 1.5 × 10^6 counts. The results of fits to averaged data always agreed to within experimental error with the averaged results of separately analyzed data. Correlation functions measured at a scattering angle of 60° and plotted against $q^2\tau$ were the same to within random errors as those measured at 90°.

Results and Discussion

Typical plots of ln y_i are shown in Figure 1. The full lines show the results of double-exponential fits excluding Δ (i.e., four-parameter fits). The concentration of component 1 increases in the order of (a) to (c). Except for a slight systematic deviation, the fits describe the data reasonably well. Typical values of the weighted sum of squared residuals were 6 × 10^{-4} for four-parameter fits and 4 × 10^{-4} for five-parameter fits. (However, it should be noted that these values were obtained with weighting factors which were normalized to 2 instead of 1 for computational convenience. This weighting makes no difference to the results of the fits since it is only a minimum in the weighted sum of squared residuals that is sought rather than its absolute value.) The inclusion of Δ as an extra fitted parameter improved the agreement between fits and data but is also increased the uncertainty (see Table II) in values of the fitted parameters. A systematic

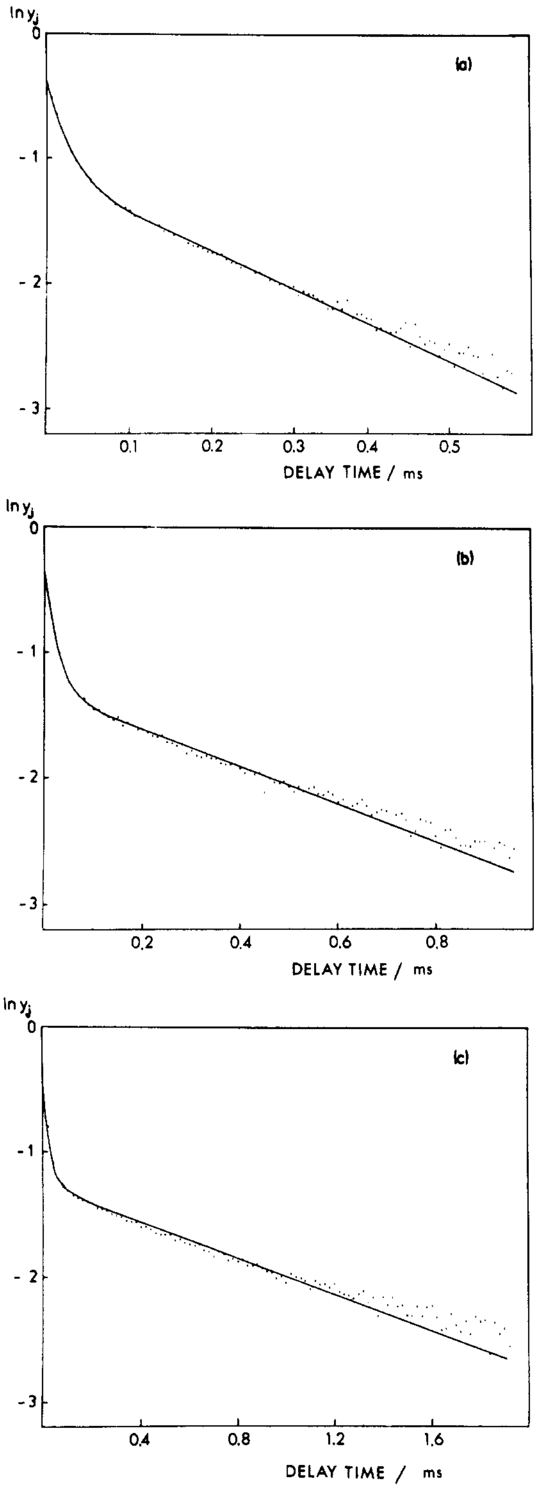

Figure 1. DLS data at θ = 90° averaged over three or four runs (points) and the corresponding results of four-parameter fits (solid curves). The concentrations of dextran T20 in kg m^{-3} are (a) 67.6, (b) 104.8, and (c) 134.2. The sample times in μs are (a) 6, (b) 10, and (c) 20.

Table II
Results of DLS Experiments: Dextran Mixtures[a]

$C_1{}^b$/kg m^{-3}	$C_2{}^b$/kg m^{-3}	$D_+/10^{-11}$ m^2 s^{-1} without Δ[c]	$D_+/10^{-11}$ m^2 s^{-1} with Δ[d]	$D_-/10^{-12}$ m^2 s^{-1} without Δ[c]	$D_-/10^{-12}$ m^2 s^{-1} with Δ[d]
46.9	5.06	7.2 ± 0.3	7.9 ± 0.4	6.5 ± 0.1	8.2 ± 0.3
67.6	5.04	7.62	7.95	5.04	6.63
73.1	5.15	7.25 ± 0.05	7.8 ± 0.2	3.52 ± 0.01	5.4 ± 0.3
94.7	5.25	8.24 ± 0.08	8.7 ± 0.3	3.7 (±0.1)	6.0 ± 0.8
104.8	5.19	7.81	8.02	2.51	3.71
110.8	5.23	7.9 ± 0.1	8.3 ± 0.2	1.95 ± 0.7	4.0 ± 0.7
134.2	5.22	9.95	8.23	1.23	2.04
134.7	5.35	7.8 ± 0.3	8.2 ± 0.3	1.7 ± 0.1	2.9 ± 0.2
150.8	5.29	8.2 ± 0.1	8.5 ± 0.1	1.14 ± 0.03	3.5 ± 0.3
166.1	5.31	8.2 ± 0.04	8.5 ± 0.5	0.90 ± 0.05	1.8 ± 0.4

[a] Uncertainties were calculated from the variation in values obtained from fits to different sets of data obtained under the same conditions. [b] Calculated from mass fractions taking the partial specific volume of dextran as 6.0 × 10^{-4} m^3 kg^{-1}.[18] [c] Results of double-exponential fits without Δ. [d] Results of double-exponential fits with Δ.

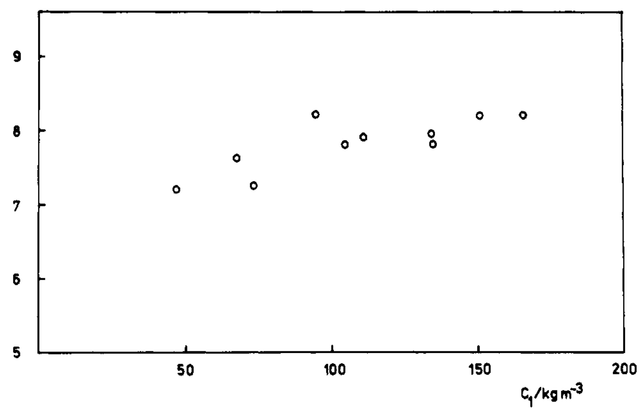

Figure 2. Values of D_+ extracted from four-parameter fits to DLS data vs. concentration of dextran T20.

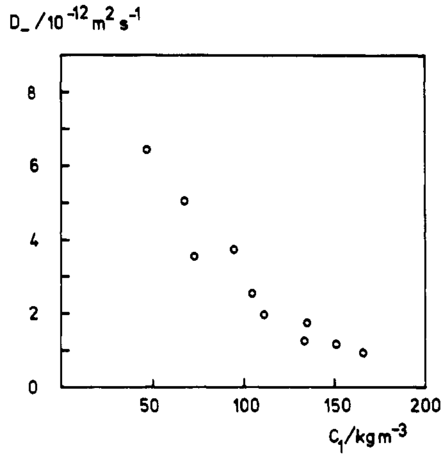

Figure 3. Values of D_- extracted from four-parameter fits to DLS data vs. concentration of dextran T20.

increase in values of Δ from 0.036 for the lowest concentration to values around 0.10 for the highest concentrations was also observed. This trend is probably due to a tendency of the double-exponential fits which include Δ to overestimate the decay rates of the exponentials and attribute the latter part of their decay to a constant base line, especially when the difference between the decay rates of the two exponentials begins to decrease. This trend has been observed in fits to synthetic data[17] and it can be seen as a consequence of having a finite data set. When there exists a genuine spread in values of the decay rates due to polydispersity for example, this effect will become more serious. For these reasons, although the results obtained for both four- and five-parameter fits are reported (Table II), further discussions will be limited to the results obtained from four-parameter fits. The values obtained from the two different fits give an estimate of the upper and lower bounds of D_+ and D_-. Typical values of γ were of the order of 0.65.

Values of D_+ and D_- obtained from four-parameter fits are plotted in Figures 2 and 3. The relative insensitivity of D_+ and rapid decrease of D_- with increasing concentration of dextran T20 are similar to the trends displayed by the mutual diffusion coefficient D_m and the self-diffusion coefficient D_s (also known as the tracer or intradiffusion coefficient) respectively, in binary polymer solutions[3] and dispersions of colloidal spheres.[6] The amplitude A of the + mode is plotted against concentration in Figure 4.

It has previously been shown[19] that the ternary diffusion coefficient D_{ij} may be evaluated from binary friction coefficients (f_{13}, f_{23}, and f_{21} in the notation of ref 19) and thermodynamic data. These calculations require knowledge of the mutual diffusion coefficients for binary dextran solutions, the intradiffusion coefficient of dextran F600 in the presence of dextran T20, and the thermodynamic nonideality coefficients. Explicit values of these coefficients or extrapolated estimates have been taken from Preston et al.[3] The results of these calculations shown in

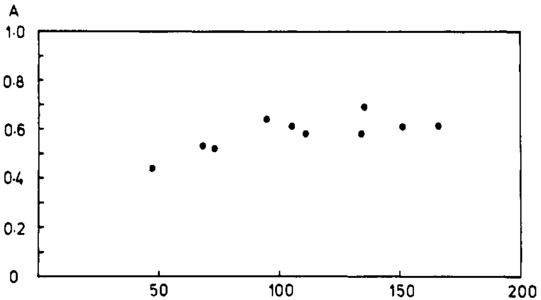

Figure 4. Values of the amplitude, A, of the + mode extracted from four-parameter fits to DLS data vs. concentration of dextran T20.

Table III
Calculated Values of Ternary Diffusion Coefficients

C_1/kg m^{-3}	$D_{ij}/10^{-11}$ m^2 s^{-1} D_{11}	D_{12}	D_{21}	D_{22}	$D_\pm/10^{-11}$ m^2 s^{-1} D_+	D_-
50.0	7.64	51.7	0.0162	1.31	7.50	1.44
75.0	7.65	57.7	0.0142	1.122	7.52	1.25
100.0	7.66	59.2	0.0124	0.840	7.55	0.95
125.0	7.66	58.7	0.0104	0.644	7.57	0.73
150.0	7.67	57.1	0.0083	0.386	7.60	0.45

Table III demonstrate that D_{22} decreases significantly with increasing concentration of dextran T20 whereas the other ternary diffusion coefficients remain relatively constant. Furthermore, the magnitude of the product $D_{12}D_{21}$ is small compared with the value of $(D_{11} - D_{22})$ so that eq 5 may be simplified to

$$D_{+} \simeq D_{11} \qquad (13)$$
$$D_{-} \simeq D_{22}$$

Simplified expressions for these diffusion coefficients may be obtained from the irreversible thermodynamic treatment[19] when $c_2 \ll c_1$ such that

$$D_{11} \simeq \frac{c_1}{f_{13}} \frac{\partial \mu_1}{\partial c_1} \qquad (14)$$

and

$$D_{22} \simeq \frac{RT}{f_{23} + f_{21}} \qquad (15)$$

where μ_1 is the chemical potential of component 1. Equation 14 is identical with that for the mutual diffusion coefficient in a binary system. This is also consistent with the strong similarity of the D_{+} values in Table III to the mutual diffusion coefficient of dextran T20 in a binary system[3] and to D_{+} values in Table II. D_m for dextran T20 was found to be independent of concentration up to 200 kg m^{-3}.[3] Equation 15 is equivalent to the intradiffusion coefficient of component 2 in the presence of component 1.[18] In the calculations of D_{22} it has been found that the major factor determining its magnitude is f_{21} which has been estimated from the intradiffusion studies of Preston et al.[3] More specifically, we have used the variation of the reduced intradiffusion coefficient (i.e., the ratio of the intradiffusion coefficient to diffusion coefficient obtained at infinte dilution) of dextran (MW ~ 150 000) with concentration as a measure of dextran F600 diffusion in dextran T20 solutions. There are likely to be major errors in this estimation which could account for the discrepancy between the calculated values of D_{-} (Table III) and the experimental values (Table II). Certainly, experimental measurements of diffusion coefficients less than 1.0×10^{-11} m^2 s^{-1}, as would be the case for D_{-}, by conventional boundary relaxation techniques are difficult and subject to relatively large errors.[20]

Conclusion

In this work it has been shown that two modes of decay of concentration fluctuations are observed in the DLS data for ternary solutions of dextran T20 and dextran F600 in water at nonzero concentrations. Encouraging agreement between calculations based on irreversible thermodynamics and DLS experiments suggests that for the concentrations used here the faster mode decays at a rate proportional to the mutual diffusion coefficient of dextran T20 and the slower mode decays at a rate proportional to the intradiffusion (or self-diffusion) coefficient of dextran F600 in the presence of dextran T20.

Acknowledgment. This work is part of a collaborative research program between Monash University and Royal Melbourne Institute of Technology, on the transport in multicomponent polymer systems, that is supported by a grant from the Australian Research Grants Scheme.

Registry No. Dextran, 9004-54-0.

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