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Photon Correlation Spectroscopy of Polystyrene Solutions

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ABSTRACT: The mutual diffusion coefficient in polystyrene solutions is examined both theoretically and experimentally. The measurements are shown to be incapable of testing the scaling law predictions for the osmotic modulus and friction coefficient. Measured values of D_c in carbon tetrachloride and ethyl acetate yield no hint of a crossover region between dilute and semidilute solutions. The mutual diffusion coefficient eventually reaches a maximum with concentration.

Concentration fluctuations in fluid mixtures lead to light scattering which can be analyzed by using photon correlation spectroscopy. The physical quantity that is determined is the mutual diffusion coefficient D_c. At infinite dilution the mutual diffusion coefficient is equal to the self-diffusion coefficient of the solute. Photon correlation spectroscopy has become a standard technique for determining the self-diffusion coefficient for polymers in solution.[1]

There has been a great deal of current interest[2-5] in the behavior of the mutual diffusion coefficient as a function of concentration. This has been stimulated by the theoretical predictions of deGennes.[6] Certain asymptotic results are obtained in the semidilute region of concentration for the osmotic pressure and for the friction per unit volume, using scaling law arguments. In the present paper we examine the validity of this approach in the description of concentration fluctuations in polymer solutions. Measurements of the mutual diffusion coefficient for 600 000 molecular weight atactic polystyrene in carbon tetrachloride and in ethyl acetate were carried out as a function of concentration.

Theory

Photon correlation spectroscopy measures the quantity

$$C(t) = \langle I(t)I(0)\rangle / \langle I(0)\rangle^2 \qquad (1)$$

where $I(t)$ is the intensity of light scattered by the sample at time t. For pure thermal density and concentration fluctuations the correlation function is given by

$$C(t) = 1 + \phi^2(t) \qquad (2)$$

where $\phi(t)$ is the relaxation function for the fluctuations which give rise to the light scattering. For all the samples studied in this work, the density fluctuations are too fast to be observed by photon correlation spectroscopy. The concentration fluctuations can be described by a relaxation function

$$\phi_c(t) = \exp(-D_c q^2 t) \qquad (3)$$

where $q = 4\pi n/\lambda \sin \theta/2$ is the magnitude of the scattering vector for light of vacuum wavelength λ in a medium of refractive index n scattered at an angle θ in the scattering plane. Because not all the scattered intensity is due to concentration fluctuations, the value of $C(t)$ at the shortest measured times will be less than 2. The exact value can be calculated from a knowledge of the fraction of scattered light associated with the concentration fluctuations. Care was taken to assure that this theoretical value was realized in practice.

The value of the mutual diffusion coefficient is determined by the restoring force for the concentration fluctuations divided by the frictional resistance

$$D_c = E_c/\Phi \qquad (4)$$

where $E_c = c\,\partial\pi/\partial c$ is the osmotic modulus and π is the osmotic pressure, and Φ is the friction per unit volume. At infinite dilution the diffusion coefficient is given by

$$D_0 = kT/6\pi\eta R_h \qquad (5)$$

where k is Boltzmann's constant, η is the solvent viscosity, and R_h is the effective hydrodynamic radius. As the concentration of polymer is increased in a good solvent, the osmotic modulus increases substantially and so does the friction per unit volume. The observed behavior of the mutual diffusion coefficient is a balance between these two effects. If we ignore the small term related to the partial specific volume of the polymer in solution, the behavior of D_c in dilute solution depends on the difference $2A_2M - k_f$, where A_2 is the osmotic second virial coefficient, M is the molecular weight of the polymer, and k_f is the second virial coefficient for the friction coefficient. For a Θ solvent, the mutual diffusion coefficient falls as the concentration is increased. In a very good solvent, D_c can increase substantially, even in dilute solution.

In order to discuss the semidilute concentration region, it is necessary to specify what is meant by semidilute. A concentration c^* is taken as the boundary between dilute and semidilute regions. It has been proposed by deGennes[6] that c^* is proportional to the polymerization index N di-

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vided by the cube of the radius of gyration of the molecule. Adam and Delsanti[2] chose the definition

$$c^* = M/N_A R_g^3 \tag{6}$$

where R_g is the radius of gyration and N_A is Avogadro's number. We will consider the consequences of the above definition in the following discussion.

It has been proposed[6] that at c^* the solution forms a pseudogel network with one temporary cross-link per chain. The rubber elastic modulus is given by

$$E_r = \nu kT \tag{7}$$

where ν is the number density of cross-links. If c^* is given by eq 6, then the rubber elastic modulus at c^* will be

$$E_r^* = kT/R_g^3 \tag{8}$$

In the semidilute region, the rubber modulus will be given by

$$E_r = kT/\xi^3 \tag{9}$$

where ξ is a correlation length equal to the distance between entanglement points, and hence the number of cross-links per unit volume is $1/\xi^3$. Because the cross-links are only temporary, it is important to examine the solution under conditions where the pseudogel will persist for sufficiently long times relative to the decay of the concentration fluctuations. The molecular weight and scattering angle were chosen in this work so that the product qR_g approached 1. Under these conditions the reptation time of the molecules in the semidilute solution should exceed $(D_c q^2)^{-1}$.

It has further been proposed that the osmotic modulus will scale like the pseudogel modulus in the semidilute region. In practice[2] this has been interpreted to mean that the two quantities are equal. The osmotic modulus can be estimated empirically by using the virial expansion. At c^* the osmotic modulus in a good solvent can be expressed as

$$E_c^* = E_r^*(1 + 2A_2Mc^* + 3A_3Mc^{*2} + ...) \tag{10}$$

where A_3 is the third osmotic virial coefficient. For a good solvent $A_3 \approx 0.3A_2^2M$. For polymers of molecular weight near 10^6 g/mol dissolved in good solvents ($A_2 \approx 4 \times 10^{-4}$ mol cm^3/g^2) with $c^* \approx 0.01$ g/cm^3, the osmotic modulus at c^* is at least 23 times as large as the proposed pseudogel elastic modulus. This suggests that the initial speculation equating E_c with E_r in the semidilute region is not valid for a good solvent. Although the two quantities may have the same scaling law far above c^*, measurements of the osmotic modulus may not reflect this asymptotic result in the experimentally accessible region for the mutual diffusion coefficient.

The friction per unit volume Φ can be separated into the number density of diffusing objects times the friction per object. At infinite dilution this is

$$\Phi = \frac{cN_A}{M} 6\pi\eta R_h \tag{11}$$

which leads to eq 5 for D_0. Even in dilute solution the friction per molecule increases substantially over the value given in eq 11, so that at c^* the infinite dilution value of Φ is a very bad choice.

In the semidilute region it has been proposed that the friction per unit volume should scale like the screening length ξ_h, which is equal to the hydrodynamic radius of part of the molecule called a blob. Predictions are then made of the number of blobs per molecule as a function of concentration. At c^* there is one blob per molecule with effective hydrodynamic radius R_h. However, at finite concentration the friction per blob may greatly exceed the infinite dilution value and a knowledge of ξ_h is not sufficient to calculate Φ. A simple formula for D_c in the semidilute range has been proposed.

$$D_c = kT/6\pi\eta\xi_h \tag{12}$$

The above arguments suggest that eq 12 is a gross oversimplification and that values of ξ_h determined from measurements of D_c with the use of this relation should be considered invalid.

In dilute solution it is possible to use the solvent viscosity to calculate the friction factor, but at higher concentrations the local viscosity will increase due to the decrease in free volume with increasing polymer concentration. Eventually the friction per unit volume in polystyrene solutions will increase faster than the osmotic restoring force and the mutual diffusion coefficient will reach a maximum and then begin to decrease. The scaling law predictions are only expected to be valid far above the crossover concentration c^*. The rapid increase in the friction per unit volume will tend to obscure the observation of a pseudogel network.

One experimental result which has been cited in support of the blob theory is the molecular weight independence of D_c in the semidilute region. The osmotic modulus is expected to become independent of molecular weight as soon as the higher terms in the virial expansion dominate its value. As shown above this will be the case above c^*. The friction per unit volume is also known[7] to be independent of molecular weight in the semidilute region. This is expected since the segment friction factor should depend only on the density of segments above c^*. Thus, the molecular weight independence is not a proof of the blob theory.

Experimental Section

Atactic polystyrene of molecular weight 600 000 was obtained from the Pressure Chemical Co. Carbon tetrachloride and ethyl acetate were of spectroscopic quality and were used without further purification. Solutions were filtered directly into the scattering cell through 0.2 μm filters. The highest concentrations were obtained by evaporating the solutions in a vacuum oven. This maintained optical purity without the need to filter the very viscous solutions.

The scattered intensities were analyzed with a Malvern correlator operated in the single clipped mode. Observed relaxation functions could be represented satisfactorily by eq 3. No attempt was made in this paper to address the interesting and potentially important issue of whether the relaxation function for concentration fluctuations is rigorously a single exponential decay.[5] The incident light was at 5145 Å and the scattering was observed at 90°.

Results and Discussion

The diffusion coefficient for 600 000 molecular weight polystyrene in carbon tetrachloride at 23 °C extrapolated to infinite dilution was found to be 1.0×10^{-7} cm^2/s. This corresponds to a hydrodynamic radius of 217 Å. It should be noted that R_h is substantially smaller than the radius of gyration which for this polymer is approximately 400 Å. The above result is consistent with previous work by Allen et al.[8] which showed that the hydrodynamic radius is observed to be in the range 0.4–0.6 times the radius of gyration. The mutual diffusion coefficient increases with concentration and near c^* is approximately 2.3×10^{-7} cm^2/s. The initial slope is consistent with the quantity $2A_2M - k_f$. The value of c^* for this system is approximately 16 mg/mL. The mutual diffusion coefficient continues to rise above c^* and reaches a maximum near 6.2×10^{-7} cm^2/s at a concentration of 150 mg/mL. A plot of D_c vs. c is shown in Figure 1. From this plot there is no

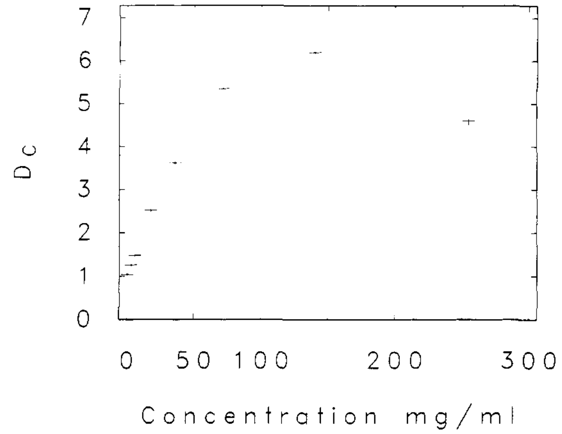

Figure 1. Plot of the mutual diffusion coefficient D_c vs. the concentration for 600 000 molecular weight atactic polystyrene in carbon tetrachloride at 23 °C.

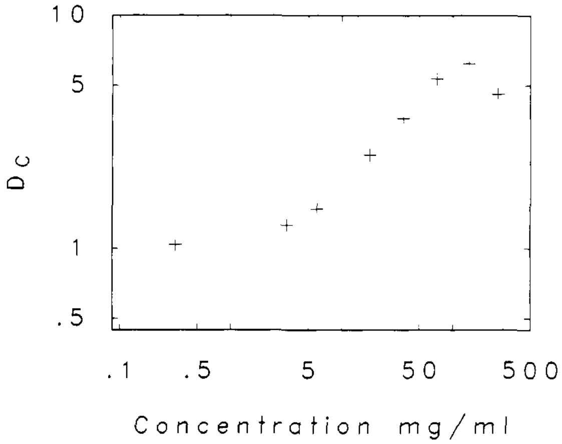

Figure 2. Log–log plot of the data in Figure 1.

hint of the value of c^*. The value of D_c rises linearly at lower concentrations and eventually falls off at higher concentrations.

It has been predicted that the mutual diffusion coefficient is described by a power law

$$D_c = Ac^B \tag{13}$$

in the semidilute region with B near 0.75. As a result the data have been plotted on a log–log plot and the slope in the semidilute region has been interpreted as the power law exponent. A log–log plot of the data is shown in Figure 2. Since D_0 is finite, there is a long nearly horizontal region which corresponds to values of D_c near D_0. The apparent crossover region is an artifact of the log–log plot. In order to obtain the power law exponent from the slope of the log–log plot, it is necessary to subtract the finite intercept from the data. The actual data are linear at the lower concentrations. These considerations cast doubt on the validity of the analysis carried out in several[2,3] previous papers.

In a previous study[4] of polystyrene in styrene, the linear increase of D_c with concentration persisted up to at least 100 mg/mL. The value of the mutual diffusion coefficient reached a maximum and then decreased, just as in this study. In a good solvent the above features seem to be characteristic of polystyrene solutions. In a poor solvent the mutual diffusion coefficient decreases with concentration initially and eventually turns around and increases with concentration before the final decrease due to the increasing local friction. Ethyl acetate was chosen as a solvent because it is intermediate between a good solvent and a poor solvent. In ethyl acetate the mutual diffusion coefficient is nearly independent of concentration in the dilute range. Above c^* the mutual diffusion coefficient does rise, but a power law description would lead to an exponent greater than 1 in the semidilute region. The value of D_c eventually reaches a maximum value near 5.8×10^{-7} cm^{-}/s at a concentration of approximately 150 mg/mL. A plot of the results is shown in Figure 3. The solvent quality has a very dramatic influence on the results, and the differences appear to be outside the ability of the blob theory to interpret them.

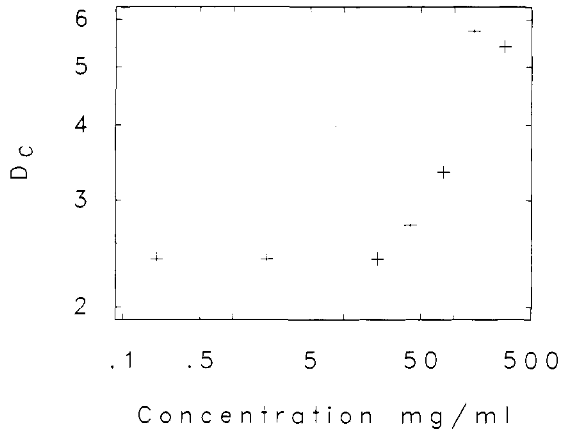

Figure 3. Plot of D_c vs. concentration for polystyrene in ethyl acetate.

The behavior of the mutual diffusion coefficient with concentration in polymer solutions is determined by a subtle balance between the osmotic restoring force for the concentration fluctuations and the friction per unit volume opposing the motion. The suggestion that the osmotic compressibility can be equated with the pseudogel elastic modulus near c^* is not correct for a good solvent. Nor is it correct to suppose that the friction per unit volume can be calculated from a knowledge of the dynamic screening length alone. The present results indicate that measurements of the mutual diffusion coefficient D_c are not a good test of the pseudogel theory of polymer solutions. The range of concentration over which such a theory would be expected to be valid appears to be too small to be observed before other effects obscure the behavior. The initial optimistic claims of agreement between theory and experiment should be re-examined.[2,3]

The present paper is intended to call attention to some fundamental inconsistencies in the treatment of the theory and measurements of the mutual diffusion coefficient. Unfortunately, it does not provide more than a qualitative picture of the behavior of the mutual diffusion coefficient of polystyrene in a good solvent. The initial linear increase of D_c with concentration and the eventual maximum place severe limits on the utility of these measurements for testing pseudogel theory. Direct measurements of the pseudogel elastic modulus in semidilute solutions should be a better test.

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