

The concentration dependence of diffusion in semi-dilute polymer solutions

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Dynamic light-scattering data for polystyrene fractions in a good solvent (benzene) and a theta solvent (cyclopentane, 20.4°C) are presented. They encompass a broad concentration interval in the semi-dilute range. These data are compared with those for the systems poly(ethylene oxide)/water and hydroxyethylcellulose/water. The entanglement network in these systems is reflected in part by the nature of the concentration dependence of the mutual diffusion coefficient and in part by the presence of a slow relaxation, information on which may be derived from the non-exponential autocorrelation function.

(Keywords: Diffusion; semi-dilute polymer solutions; concentration dependence; polystyrene; poly(ethylene oxide))

INTRODUCTION

A previous paper¹ dealt with a comparison of self-diffusion data, obtained using pulsed-field-gradient n.m.r., for poly(ethylene oxide)s in semi-dilute solutions with a slow relaxation mode observed in dynamic light scattering. The slow relaxation, which is manifested in the non-exponential nature of the determined autocorrelation function at higher concentrations, was found to be between one and two orders of magnitude slower than self-diffusion but to have a similar concentration dependence.

The complementary fast relaxation which is considered to characterize cooperative diffusion of the transient network in semi-dilute systems is known to increase in frequency with concentration in good solvents. The dependence of the mutual diffusion coefficient, D , on concentration is determined by the balance between the osmotic restoring force for the concentration fluctuations divided by the mutual friction:

$$D = \frac{c(\partial\pi/\partial c)_{TP}}{f} \quad (1)$$

where π is the osmotic pressure and f the friction per unit volume. D increases with increasing concentration until the rapidly increasing friction as the solution becomes concentrated balances the osmotic modulus; D should thus pass through a maximum as has been observed experimentally by Patterson *et al.*³ and Schaefer *et al.*⁴ for polystyrene in various solvents. This plateau feature of the entanglement network is shown below to be associated with the appearance of a slow relaxation in the system. Data are presented and discussed for the polystyrene/benzene, poly(ethylene oxide)/water and hydroxy ethyl cellulose/water systems. The importance of defining the dynamical regime when using dynamic light scattering is

emphasized in the literature⁵. The molar masses of the samples were thus chosen so that measurements are within the $qR_G < 1$ and $C/C^* > 1$ sector and should be essentially independent of internal motions of the polymer coil.

EXPERIMENTAL

Polymers

Polystyrenes. Narrow distribution polystyrenes PS 110 ($M = 1.10 \times 10^5$; $\bar{M}_w/\bar{M}_n < 1.06$) and PS 390 ($M = 3.9 \times 10^5$; $\bar{M}_w/\bar{M}_n < 1.08$) were purchased from Pressure Chemical Co., Pittsburgh, Pa, USA.

Poly(ethylene oxide). SE-70 ($M = 6.61 \times 10^5$; $\bar{M}_w/\bar{M}_n < 1.10$) was from Toya Soda Ltd, Tokyo, Japan.

Hydroxyethylcellulose. Fraction C-8, has been described in ref. 6; $\bar{M}_w = 5.15 \times 10^5$; $\bar{M}_n = 3.8 \times 10^5$.

Solvents and solutions

Benzene. This was chromatographic grade from Merck, Darmstadt, FRG. It should be noted that the earlier reported measurements on semi-dilute solutions of polystyrene in toluene¹ and subsequent measurements in benzene revealed the presence of a slow relaxation in dynamic light scattering at temperatures below 20°C and which 'melted-out' at higher temperatures. It was found that this effect was due to the presence of traces of moisture in these solvents. The log D vs. log C plots reveal, for example, a characteristic depression which has been described by Chu and Nose^{1,7}, and is apparently related to critical effects. The solvent was thus dried exhaustively over freshly treated (350°C; high vacuum) molecular sieves (3 Å; Union Carbide). With this treatment the slow relaxation was not apparent at low temperatures (down to 5°C). Most reports dealing with measurements in semi-dilute solutions in these solvents fail, however, to mention the necessity of rigorous drying procedures.

It is also extremely difficult to prepare dust- and particle-free solutions of polymers at high concentration. We achieved this by construction of a closed-circuit filtration unit. A 10 ml syringe, driven by a low-g geared motor and directionally controlled by micro-switches and magnetic valves, repeatedly emptied a small volume of solution through a 0.22 μm Fluoropore filter (Millipore) which was then returned via a reservoir to the syringe. After some hours of very slow filtration, completely optically clear solutions of up to 20% (w/w) polymer were obtained. The absence of dust and aggregated material in the present solutions was checked by measurements of the angular dependence of the scattering intensity. After the usual angle correction, an angular-independent photocount was obtained.

Dynamic light scattering and data treatment

The experimental arrangement has been described previously⁷ and the main features only are summarized here.

The light source was a Coherent Radiation, model CR-4, argon-ion laser containing a quartz etalon frequency stabilizer in the cavity to ensure single-mode operation at 488 nm. The detector system comprised an ITT FW 130 photomultiplier, the output of which was digitized by a Nuclear Enterprises amplifier/discriminator system. A Langley-Ford 128-channel autocorrelator was used to generate the full autocorrelation function of the scattered intensity. All experiments were performed in the homodyne mode. The correlator was interfaced to a Luxor ABC-computer, programmed to calculate the normalized full photon counting time correlation function and the data stored on floppy discs. The measurements were made at an angle of 90° and at 25°C except where otherwise specified.

The full photon counting time autocorrelation function was analysed by the method of cumulants⁸. Thus $\ln|g^{(2)}(\tau) - 1|$ versus τ was fitted with appropriate weighting in a linear regression program to a second-order equation. The first coefficient equals $(-2\bar{\Gamma})$ and the second (μ_2) , where $\bar{\Gamma}$ is the average inverse relaxation time and its variance is $\mu_2/\bar{\Gamma}^2$:

$$\ln|g^{(2)}(\tau) - 1| =$$

$$\ln \beta + 2 \left[-\bar{\Gamma}\tau + \frac{1}{2!} \left(\frac{\mu_2}{\bar{\Gamma}^2} \right) (\bar{\Gamma}\tau)^2 - \frac{1}{3!} \left(\frac{\mu_3}{\bar{\Gamma}^3} \right) (\bar{\Gamma}\tau)^3 + \dots \right] \quad (2)$$

and β is an adjustable parameter in the data-fitting procedure.

The intensity correlation function was in some cases (see Figures 3, 6 and 9) clearly the sum of two exponential functions, where the gamma values were in the ratio of approximately 100:1. It was thus necessary to make two experiments on each solution using sampling times differing by a factor ≥ 100 . The sampling time was chosen so that the 120 channels covered 2–4 relaxation times in the observed exponential process. With the slow process it was necessary to discard the data for the shortest correlation times; thus the first ten points were rejected. In the case of the fast component the experimental baseline was used; the correlator also allows the last 8 channels to be delayed so that the last channel corresponds to a delay time of 256 channels. In the case of the slow component (long sampling time) the infinite time baseline was em-

ployed. The measured quantity, $\bar{\Gamma}/q^2$, did not show a systematic variation with scattering angle for the fast and slow relaxations, $\bar{\Gamma}_f$ and $\bar{\Gamma}_s$.

The amplitude ratio corresponding to the two modes is dependent on angle, however. A_f/A_s increases linearly with increasing angle from 0.14 ($\theta = 70^\circ$) to 0.40 ($\theta = 110^\circ$) for PS 110 at $C = 20.3\%$ (w/w).

Fourier transform pulsed-field-gradient n.m.r.

These measurements have been described previously^{1,9} and the procedure was that detailed by Stilbs¹⁰.

RESULTS AND DISCUSSION

Polystyrene/benzene

Data are shown in Figure 1 for two fractions ($M = 1.1 \times 10^5$ and 3.9×10^5). The concentration designated C^* is arbitrarily defined here¹¹ as:

$$C^* = \frac{M}{(4/3)\pi R_G^3 N_A} \quad (3)$$

where the polymer coil is viewed as occupying a sphere of radius R_G . An alternative bound is defined¹² as:

$$C^+ = \frac{M}{R_G^3 N_A} \quad (4)$$

In a good solvent, as here, the mutual diffusion coefficient increases with concentration and there is typically no sign of a discontinuity as C^* is passed.

As shown by Patterson *et al.*³, one anticipates that D will pass through a maximum at higher concentrations and eventually decrease as the friction per unit volume increases and finally dominates over the osmotic restoring force. This maximum is apparent for the higher molecular weight fraction and has also been observed for this material in the solvents ethyl acetate and THF by Schaefer *et al.*⁴; it presumably signals the concentrated region. A point of difference which contradicts the predictions of the pseudogel theory, however, is that above C^* there is a clear, if small, dependence of D on

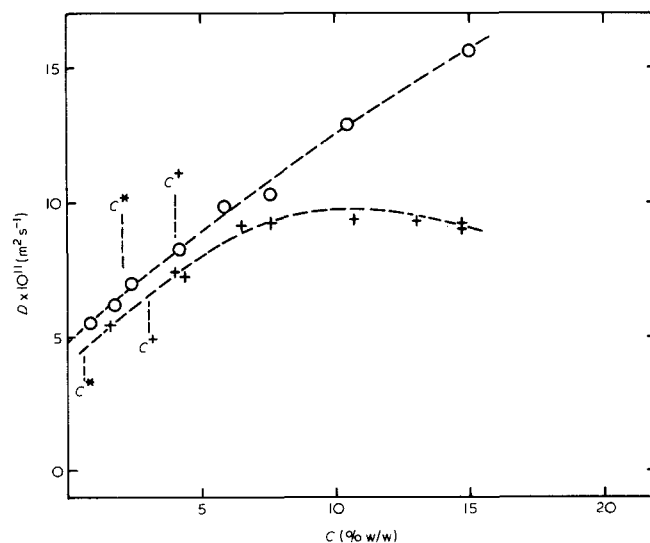


Figure 1 Mutual diffusion coefficients versus concentration for solutions of polystyrene in benzene at 25°C: O, $M = 1.1 \times 10^5$; +, $M = 3.9 \times 10^5$

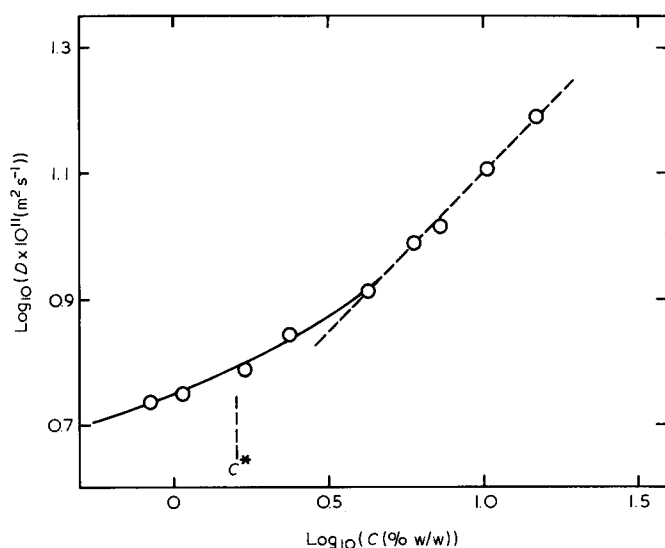


Figure 2 Log-log plot of the data ($M=1.1 \times 10^5$) from Figure 1; the dotted line has a slope 0.50

molar mass observable in Figure 1, which is similar in magnitude to that noted by Bailey *et al.*¹³ for polystyrene in the marginal solvent 2-butanone.

Figure 2 is the familiar log-log plot employed in scaling for the PS 110 ($M=1.1 \times 10^5$) fraction. The broken line has a slope of 0.50 to be compared with a theoretical value⁵ of 0.75. The present value may be compared with a slope of 0.67 determined by Adam and Delsanti¹² in the same solvent. There are extensive data in the literature (see, for example, ref. 28) pointing to an exponent of 0.5. The value of the exponent is, of course, influenced by the quality of the solvent and the extent to which the friction per unit volume is manifest in the particular system. In a marginal solvent, an exponent of 0.5 is anticipated³⁸. It has been argued that working with larger molecular weights may lead to a validation of the scaling exponent 0.75. However, it is clear from Figure 1 that the frictional interactions will then possibly even more severely curtail the concentration range in which the predicted scaling law might be observable. Patterson and coworkers³ have pointed out that the crossover region displayed in Figure 2 is an artefact of the log-log plot and that the actual data are in fact linear at the lower concentrations as seen in Figure 1.

A further and complicating aspect is the appearance of a slow relaxation concomitant with the increasing dominance of friction shown in Figure 1 for PS 390. These data are shown in Figure 3. At above 10%, a slow relaxation ($\bar{\Gamma} < 10 \text{ s}^{-1}$) becomes observable, where $\bar{\Gamma}$ is the mean inverse relaxation time obtained in cumulant analysis⁸ of the autocorrelation function. The non-exponential character of the autocorrelation function has been noted by a number of workers^{13,15-23} and investigated in detail by Chu and Nose^{15,17}. It cannot be explained in terms of polydispersity effects but instead demonstrates the presence of additional relaxation modes, although their origin is still a question of speculation. Thus it is not known why a slow relaxation may manifest itself in some systems but not in others and why it appears at relatively low concentrations in polar and polyelectrolyte systems and at higher concentrations in non-polar systems. Amis *et al.*²² and Amis and Han²³ have related the slow relaxation to self-diffusion but this is unlikely; a comparison¹ of D values obtained from the slow relaxation

with independently determined self-diffusion coefficients (pulsed-field-gradient n.m.r.) has shown that the latter represents a considerably faster process. The disentanglement time for a network using the reptation model can be estimated from the relationship⁵:

$$T_R = \left(\frac{6\pi\eta_0}{k_B T} \right) R_G^3 (C/C^*)^{1.5}. \quad (5)$$

For polystyrene ($M=3.9 \times 10^5$) at a concentration of 14.7% one may estimate: $T_R = 10^{-2}$ s. For comparison, the respective decay times τ_f and τ_s are 10^{-5} s and 0.3 s. Thus $\tau_f \ll T_R \ll \tau_s$.

Amis and Han²³ draw the conclusion that for correlation times greater than T_R the centre-of-mass displacements of coils will be statistically independent and postulated that self-diffusion coefficients would then be obtained from dynamic light scattering. Reihanian and Jamieson¹⁶ also note that, attendant to the onset of entanglement behaviour, there is a transition from a single-exponential form to non-exponentiality of the correlation function. As described in earlier communications^{1,22,23}, by employing a judicious choice of sampling times, one can effectively resolve the fast and slow relaxations (assuming a bimodal distribution). In the present case, sampling times differing by $\geq 10^4$ were required to provide optimal resolution of the components shown as D_f and D_s in Figure 3.

The slow relaxation is considered³⁰ to reflect the

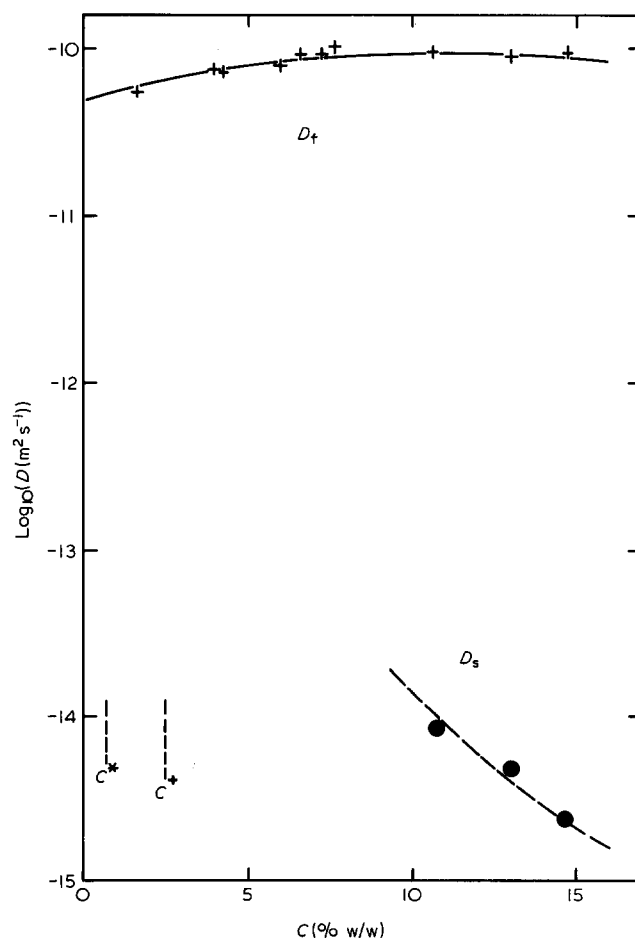


Figure 3 Semi-log plots of D versus C for polystyrene ($M=3.9 \times 10^5$) in benzene: +, fast mode; ●, slow mode

translational diffusion of intermolecularly interacting (in this case, entangling) coils; it decreases in frequency with increasing concentration and as the local viscosity increases.

From the intercepts of the cumulant treatment⁸ of the correlation data, it is possible to evaluate the amplitudes of the fast and slow components, A_f and A_s , as a function of the concentration. The fractional intensity amplitude ($A_f/(A_s + A_f)$) varied from 0.08 (at 10.7%) to 0.37 (at 14.7%) at a measurement angle of 90°. It may be noted that the fractional amplitude shows a small decrease with increasing temperature (0.3 at 25°C to 0.2 at 38°C for PS 390 at 10.7%). This effect is most likely the result of the change in R_G with a corresponding displacement in the qR_G vs. C/C^* plane; see ref. 17 for a discussion.

Temperature dependence. It may be noted that one of the conditions stipulated⁵ for the semi-dilute regime is that the friction coefficient is directly proportional to the solvent viscosity, η_0 , as implied by the relationship:

$$D = \frac{k_B T}{6\pi\eta_0\xi} \quad (6)$$

where ξ is the hydrodynamic screening length, i.e. the average distance between entanglement points in the transient network, k_B is the Boltzmann constant and T the absolute temperature. Some elucidation of this point can be obtained by examining the temperature dependence of diffusion. Figure 4 yields the following values for the apparent activation energies of PS 390 at a monomer concentration of 10.7%: $E_{D(\text{fast})} = 15 \text{ kJ mol}^{-1}$, $E_{D(\text{slow})} = 21 \text{ kJ mol}^{-1}$. On comparing these values with the activation energy for viscous flow of the solvent, $E_A = 10.2 \text{ kJ mol}^{-1}$ (obtained from the temperature dependence of η_0^{-1} using data from ref. 14), it is clear that these relaxations in a congested system are, as expected, influenced by the effects of entanglements, as predicted by Patterson *et al.*³, and there is divergence from the simple proportionality to the inverse solvent viscosity as in (6).

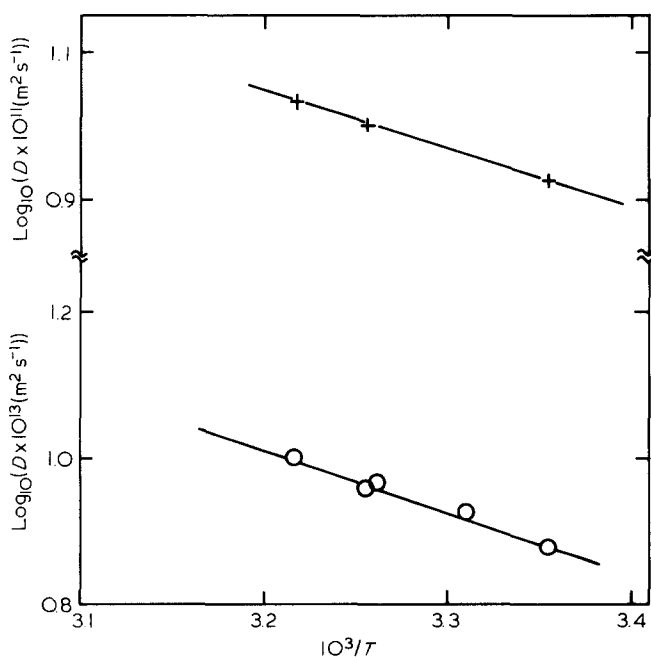


Figure 4 Arrhenius plots ($\log_{10}D$ versus $10^3/T$) for polystyrene ($M = 3.9 \times 10^5$) in benzene at a concentration of 10.7% (w/w): +, fast mode; O, slow mode (see text)

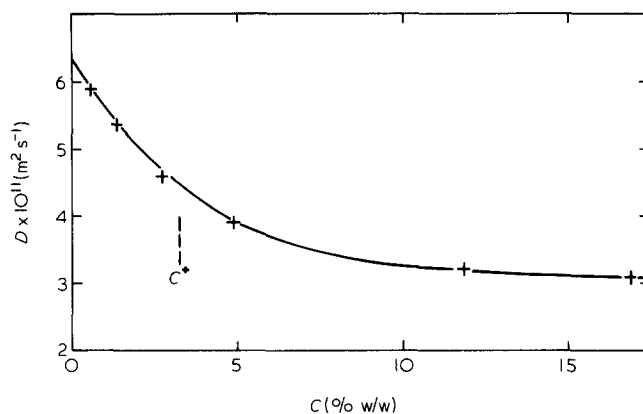


Figure 5 D versus concentration for polystyrene ($M = 1.1 \times 10^5$) in cyclopentane at 20.4°C (θ conditions)

Polystyrene/cyclopentane (20.4°C, θ conditions)

In a theta solvent (Figure 5) D decreases with concentration and mainly reflects the concentration dependence of the frictional term in equation (1). This has most recently been demonstrated by Munch *et al.*²⁴ for the presently considered system. Although this concentration dependence and that for self-diffusion are qualitatively similar in appearance, it has been established both theoretically^{25,26} and experimentally^{9,32} that the friction coefficients in mutual diffusion and self-diffusion are not identical at finite concentrations. It is relevant that only a single relaxation mode can be detected within the concentration interval examined. This is interpreted as meaning that significant inter-coil entanglement does not readily occur in a system already dominated by intramolecular interactions²⁷. This is also well illustrated by a comparison of aqueous systems described below.

Poly(ethylene oxide)/water

Data from self-diffusion measurements (pulsed-field-gradient n.m.r.) and dynamic light scattering have recently been presented^{1,9,30} for a range of molecular weights of poly(ethylene oxide) in aqueous solution. Some comparisons with the polystyrene/benzene systems may be made. In general, the same phenomena are present although they occur at lower concentrations in aqueous systems. Thus, for example, the slow relaxation analogous to that observed in the PS 390/benzene system above a concentration of about 10% becomes evident in the PEO 660/water system already at a concentration of 0.4% as illustrated in Figure 6. The latter data have been presented in a recent communication³⁰.

Self-diffusion data⁹ are shown in Figure 7 for PEO 660/water. Scaling theory⁵ predicts that D^* should be concentration-independent up to C^* and thereafter decrease according to the power law:

$$D^* \sim C^{-1.75} \quad (7)$$

Figure 7c is a log-log representation of the data. Below C^* there is a definite concentration dependence ($D^* \sim C^{-0.35}$) and above C^* , $D^* \sim C^{-1.25}$. It is noted that an alternative approach of Doi and Edwards³⁴ suggests an exponent of -1.2 for equation (7). The comments of Patterson *et al.*³ also have validity in this case; i.e. the apparent crossover region at C^* is an artefact of the plot.

It is difficult to confirm or refute the hypothesis that a slope of -1.75 will be found when samples of sufficiently

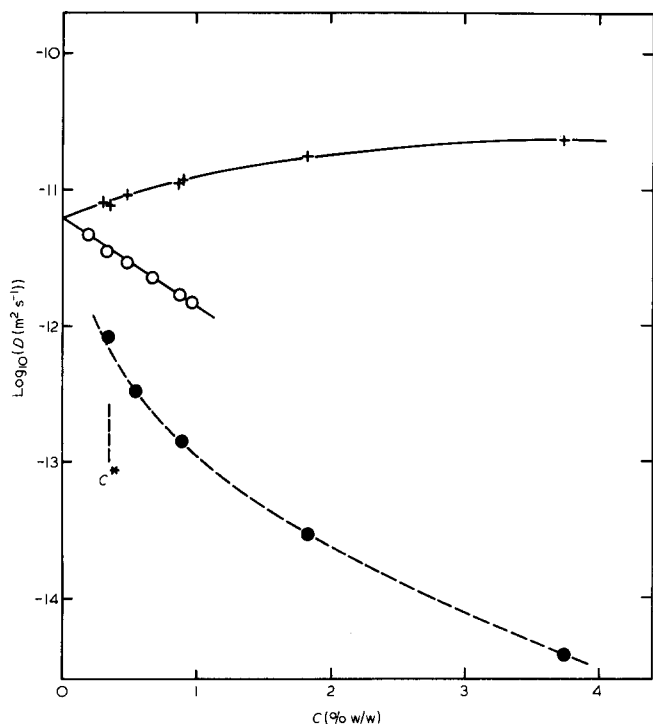


Figure 6 Semi-log plots of D versus C for poly(ethylene oxide) ($M=6.6 \times 10^5$) in aqueous solution at 25°C: x, fast mode; O, self-diffusion; ●, slow mode

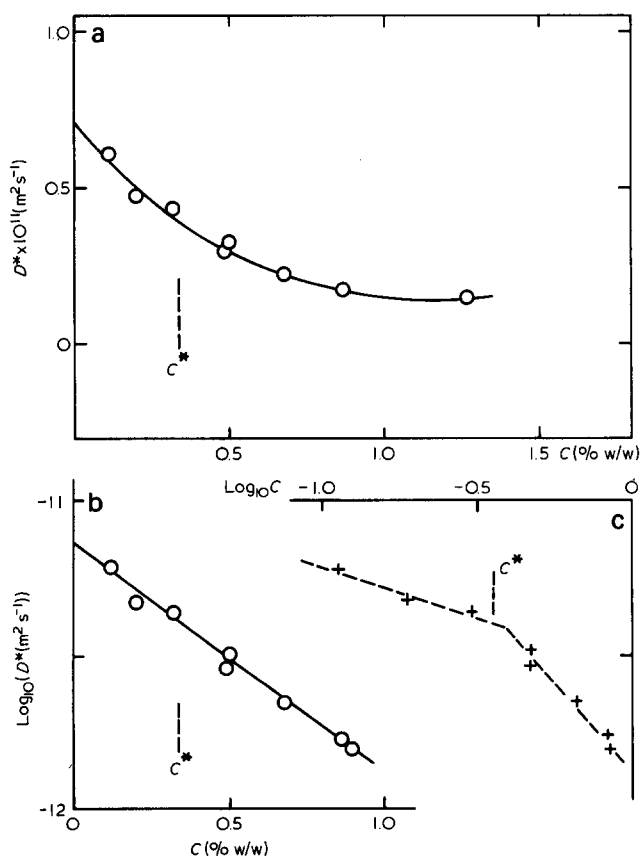


Figure 7 Self-diffusion data for poly(ethylene oxide) ($M=6.6 \times 10^5$) in aqueous solution: (a) D^* vs. C ; (b) $\log_{10} D^*$ vs. C ; (c) $\log_{10} D^*$ vs. $\log_{10} C$. The respective slopes are -0.35 and -1.25

high molar mass are used since the measurements are then associated with an unacceptably low precision using most current techniques and the data often reveal a striking curvature, suggesting that the exponent is a function of concentration, which persists to the highest concentrations in the log-log plots and this unavoidably allows subjective curve-fitting. However, it may be noted that Léger *et al.*³⁵ deduce a limiting slope of -1.7 for the PS/benzene system.

As noted before^{1,9}, the self-diffusion coefficient is found to decrease exponentially with increasing concentration and does so at all values of M investigated in the PEO/water system. The concentration dependence also increases with increasing M as is expected. When the data are normalized and plotted as shown in Figure 8, according to $\log(D^*/D_0)$ vs. $\log(C/C^*)$, a common curve is obtained for the various samples indicated. (The primary data have been discussed in ref. 9.) This demonstrates that the data are internally consistent. However, these data differ qualitatively from those of Léger *et al.*³⁵ who found that the concentration dependence is independent of M in the semi-dilute region. This would suggest that the present data are more typical of the 'crossover' range and that higher molar mass samples are required to explore the range of validity of equation (7).

Hydroxyethylcellulose/water

Further measurements were made on hydroxyethylcellulose, a macromolecule which is known to display an unusually high extension and stiffness for a non-ionic polymer. The data shown in Figure 9 show that a slow relaxation is present down to very low concentrations. The fractional intensity amplitude $A_s/(A_s + A_f)$ varies from 0.45 at 0.19% to 0.80 at 0.53%. This system may be contrasted with dextran ($M=7 \times 10^4$) in water. In this case on a single relaxation mode was observed³⁶ at concentrations as high as 26% w/w. Since dextran typifies an extremely compact macromolecule due, in part, to branching, the influence of chain geometry is evident.

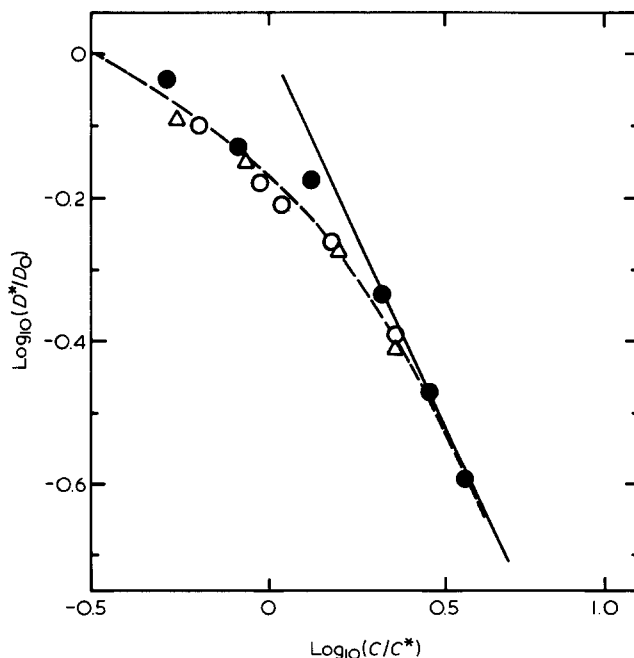


Figure 8 Plots of $\log_{10}(D^*/D_0)$ vs. $\log_{10}(C/C^*)$ for three PEO fractions in aqueous solution: Δ , 7.3×10^4 ; O, 1.48×10^5 ; ●, 6.61×10^5 . The asymptotic line has a slope of -1.25

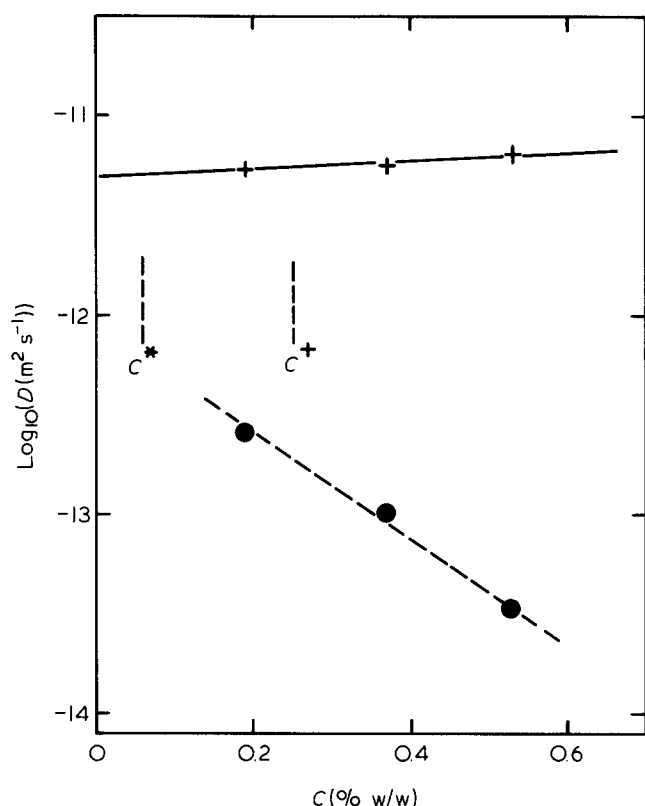


Figure 9 Semi-log plot of D versus C for hydroxyethylcellulose ($M=5.15 \times 10^5$) in aqueous solution at 25°C: +, fast mode; ●, slow mode

Fried *et al.*³⁷ have recently described the dynamic light scattering from another cellulose derivative, cellulose tricarbanilate, exhibiting a high intrinsic extension. They find a mean persistence length of 170 Å compared with a value of 83 Å for hydroxyethylcellulose. Fried *et al.*³⁷ similarly describe a slow relaxation which increases with concentration, but also diminishes with increasing temperature. This they attribute to the diffusion of entangled structures which could constitute the precursors of an anisotropic phase.

CONCLUSIONS

The semi-dilute region appears to be more complex than previously supposed. For example, the pronounced curvature in the D vs. C plots and the simultaneous development of bimodal relaxation behaviour are not only aspects which severely limit the concentration range in which existing theories of mutual and self-diffusion in semi-dilute solutions may be expected to apply, but are also features which manifest themselves in different regions of this concentration range, depending on the polymer, its molecular weight, the chain geometry, the nature of the polymer interactions with the medium (solvent quality, specific solvent interactions), etc.

The behaviour, which in the case of polystyrene in benzene seems to typify crossover to the concentrated region, appears in the polyethylene oxide and hydroxyethylcellulose/water systems in the crossover from dilute to semi-dilute. These differences greatly restrict the general applicability of current theories of diffusion for semi-dilute solutions.

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