Probe diffusion in polymer solutions in the dilute/semi-dilute crossover regime:
1. Poly(ethylene oxide)

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The Stokes–Einstein relationship has been tested for a system of polystyrene particles sedimenting through solutions of poly(ethylene oxide) (PEO) in the dilute and semi-dilute regimes. The behaviour of three different sizes of probe particles in PEO of molecular weights 112300, 450000 and 615000 was studied by the technique of ultracentrifugation, both in the presence and absence of the non-ionic surfactant Triton X-100. Deviations from Stokes–Einstein behaviour were estimated by comparison of the microscopic viscosity experienced by the particles, calculated from sedimentation measurements, and the macroscopic viscosity of the solution, measured independently. Deviations were found to be greatest for the smallest particles, and in all cases the sense of the deviations were in the sense of the particles experiencing a greater resistance to motion than expected from Stokes–Einstein behaviour.

(Keywords: probe diffusion; solution; poly(ethylene oxide); microscopic viscosity; sedimentation)

INTRODUCTION

This paper is concerned with the transport of probe particles in solutions of poly(ethylene oxide) (PEO) in the dilute/semi-dilute crossover regime. Theoretical models[1–5], define this concentration region between dilute and concentrated as occurring above a critical concentration, C^* (g ml^{-1}) when neighbouring polymer coils overlap to form a transient mesh of polymer chains. Below this concentration, regions of pure solvent occur between those regions which are characterized by the radius of gyration, R_g, of the polymer. At C^*, the polymer coils are envisaged as just touching. One can therefore write a relationship between R_g and C^*:

$$R_g = \left(\frac{3M_w}{4N_A \pi C^*}\right)^{1/3} \qquad (1)$$

where M_w is the molecular weight of the polymer and N_A is Avogadro's number[6]. The distance between contact ('entanglement') points of the chains defines a scaling length ξ known as the correlation length. This parameter can be thought of as the characteristic dimension of the mesh. The value of ξ decreases with increasing polymer concentration above C^* according to the expression[5]:

$$\xi = R_g(C^*/C)^n \qquad (2)$$

Scaling theory requires that ξ is independent of molecular weight which implies [using equation (1)] that $n = 0.75$ for neutral polymers[5]. At C^*, $\xi = R_g$. For polymers of high molecular weight, ξ is much less than the total chain length and chain ends are rare. Above C^*, the dynamics of polymer solutions are largely controlled by the chain entanglements, with the motion of any given polymer molecule being greatly hindered by segments of other polymer molecules. However, because ξ is independent of molecular weight, it is predicted that local properties will not depend on the molecular weight and there should be a universal behaviour when concentration is expressed in terms of C/C^*.

When spherical probe particles move through an entangled solution, their motion will be affected by the presence of the transient polymer mesh. The diffusion of a probe particle of radius R in the semi-dilute regime is considered[7] to be a function of R/ξ. The Stokes–Einstein relation ($D = kT/6\pi\eta R$) for the probe particle, which relates the diffusion coefficient of the particle, D, to the viscosity of the solvent, η, will break down if the microscopic viscosity experienced by the probe particles is not the same as the macroscopic viscosity measured experimentally. This will be the case for particles of radius $R \ll \xi$, since the probe will be essentially unaffected by the presence of polymer during much of its motion. In this case, the appropriate microviscosity is likely to be close to that of the pure solvent.

It should be noted that equation (2) only identifies a characteristic length associated with the mesh. The size of the gaps in the mesh, through which the probe particle attempts to move, will be characterized in practice by some distribution. In addition, the movement of the polymer chains comprising the mesh means that the network as a whole is constantly fluctuating. This means that not only will an individual pore in the mesh have a finite lifetime but within its lifetime its size will be varying.

Langevin and Rondelez[7], in their seminal early work, have studied the sedimentation behaviour of ludox (silica) particles and a range of viruses in PEO solution by analytical ultracentrifugation. They fitted their data to a stretched exponential of the form $S/S_0 = \exp(-AC^{\nu}R^{\delta})$, where S_0 is the sedimentation coefficient of the probe extrapolated to zero polymer concentration, C is the concentration of the polymer solution, R is the radius of the probe particle, A is a constant, $\nu = 0.5$ and δ is taken

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as 1. Most of the work on probe diffusion has, however concentrated on polyelectrolyte systems[8-12]. These are difficult to interpret in a simple way because of the complexity of systems where charges are present, and the difficulty of knowing both the scaling behaviour and the absolute magnitudes of the various lengths involved (R_g, ξ, etc.). However one basic conclusion was that δ was actually zero rather than unity. In this study we have chosen to concentrate on the neutral and well-characterized polymer PEO, with monodisperse polystyrene (PS) latex particles as the probe. The validity of the Stokes–Einstein law has been examined using sedimentation in an ultracentrifuge in the presence and absence of the non-ionic surfactant Triton X-100. This same system has been previously studied by Ullmann *et al.*[13,14], using the technique of photon correlation spectroscopy (p.c.s.) to measure the diffusion coefficient. However there are notable differences between our results and the earlier work.

EXPERIMENTAL

Poly(ethylene oxide) was supplied by Polymer Laboratories. Three molecular weights were used, 112 300, 450 000 and 615 000, with M_w/M_n ratios of 1.03, 1.03 and 1.1, respectively. The samples will be designated PEO 112300, PEO 450000 and PEO 615000. The PEO was dissolved in triply distilled water with gentle agitation at room temperature. Experiments were carried out between 20 h and 48 h of the solutions being prepared. Weakly negatively charged PS latex spheres (persulphate initiated), were obtained from Bangs Laboratories[15] with radii of 32 ± 9 (PS32), 65 ± 15 (PS65) and 447 ± 6 nm (PS447), as determined by electron microscopy (data supplied by manufacturer), and p.c.s. using a Malvern System 4700c sub-micron particle analyser. The surface charge on the smallest of these was quoted by the manufacturer as ~0.004 meq g^{-1}. In each experiment, the smallest weight fraction of particles still measurable in the ultracentrifuge was used in order to minimize interparticle interactions. These values were 1×10^{-3} for the 32 nm probes, 5×10^{-4} for the 65 nm probes and 1×10^{-4} for the 447 nm probes. Poly(ethylene oxide) is known to adsorb onto the surface of PS latex in a configuration of trains, loops and long tails[16,17] which extend far into solution. For some samples, therefore, Triton X-100 [poly(ethylene glycol)-*p*-isooctyl phenyl ether, with 10 ethylene glycol units] supplied by Aldrich Chemical Co. Ltd, was added to the particle suspensions in order to prevent adsorption of PEO. These samples were prepared by careful addition of polymer solution to a suspension of PS particles in a 0.01% solution of Triton and were used as soon as possible after preparation. The hydrodynamic radii of the particles in the Triton–PEO solution did not vary with time, indicating that the Triton layer was not displaced by the PEO. The Triton layer thickness was estimated (using the Malvern System 4700c sub-micron particle analyser) to be ~2 nm, in agreement with the previous measurements of Ullmann *et al.*[13].

Sedimentation experiments were performed in a Beckman model E machine equipped with Schlieren optics and a free-running RITC temperature measuring facility[18]. Different rotor speeds, 4000–50 000 rev min^{-1}, gave the same sedimentation coefficient within experimental error. It was assumed that sedimentation of the polymer could be neglected at these speeds (this was found to occur only at much higher rotor speeds) and that sedimentation of the particles could therefore be considered as through a uniform solution at rest. A plot of reciprocal sedimentation coefficient of PS particles against polymer concentration, at low polymer concentration, enabled the sedimentation coefficient in the absence of polymer, S_0, to be obtained by linear extrapolation. The most extensive studies were carried out on PEO 615000, for which the behaviour of all three particle sizes was studied. For the remaining two molecular weights, only the sedimentation of the smallest particle (PS32) was examined, for which the deviations from Stokes–Einstein behaviour would be expected to be most marked. No additional peaks appeared in the sedimentation runs when PEO was present, indicating the absence of unexpected PEO–latex particle interactions such as dimers due to bridging.

Macroscopic polymer solution viscosities were measured using an Ostwald viscometer in a thermostatically-controlled water bath at 25.0 ± 0.02°C. From viscosity measurements, values of C^* can be obtained from plots of C/η_{sp} *versus* C, where η_{sp} is the specific viscosity; C^* is given by the reciprocal of the intrinsic viscosity (the intercept of the above plot). The values obtained were 8.73 g l^{-1} for PEO 112 300, 3.85 g l^{-1} for PEO 450 000 and 2.44 g l^{-1} for PEO 615 000. These values are in good agreement with data supplied by Polymer Laboratories.

RESULTS

The data is presented here as a plot of the relative viscosity against concentration. The absolute viscosity can be calculated from the sedimentation coefficient, S, which relates the particle radius, R, the densities of the particle and solution, ρ_p and ρ_s, respectively, and the solvent viscosity, η_s, via equation (3):

$$S=\frac{2}{9}\frac{(\rho_p-\rho_s)R^2}{\eta_s} \tag{3}$$

The calculated relative viscosity experienced by the particles, η_c, is then given by

$$\eta_c=\frac{\eta_s}{\eta_o}=\frac{(\rho_p-\rho_s)S_o}{(\rho_p-\rho_o)S_s}\sim\frac{S_o}{S_s} \tag{4}$$

where the subscript o denotes the absence of polymer, S_o being obtained by extrapolation as mentioned previously. Note that this corresponds to a microviscosity. This equation assumes that R is constant over the range of concentrations studied, i.e. with no change in the adsorbed layer thickness with concentration. This seems reasonable since the concentrations employed were well above the plateau for adsorption[17,19] so that an increase in concentration does not lead to an increase in the adsorbed amount. However the assumption will be examined further below. Cohen-Stuart *et al.*[17] have measured the adsorbed layer thickness of PEO on PS particles using p.c.s. and their data correspond to $\sim25\pm3$, 75 ± 5 and 95 ± 10 nm for the polymers used in our study of $M_w=112\,300$, 450 000 and 615 000, respectively.

The density correction factor of equation (4) was found to be extremely small and could not be reliably measured using a standard (7 ml) pycnometer. Thus ρ_s was not corrected from the density of water over the PEO

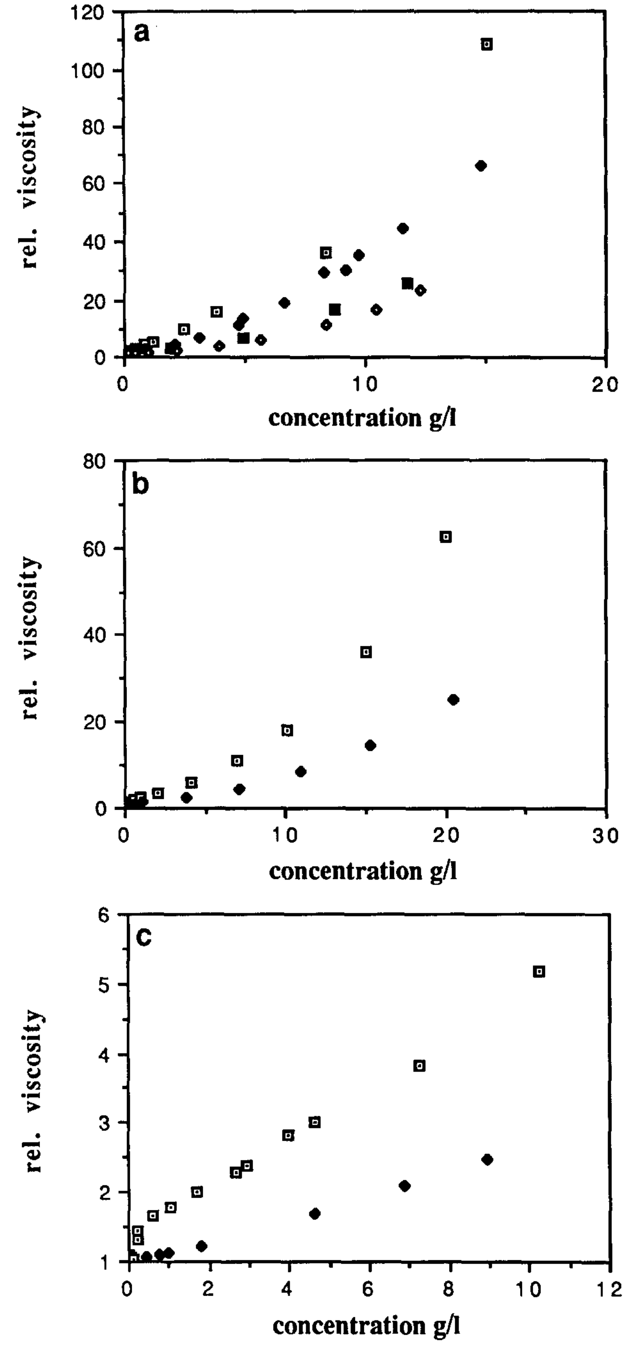

Figure 1 Comparison of the experimentally determined macroscopic and microscopic relative viscosities in (a) PEO 615000 with probe sizes of 32 (□), 65 (◆) and 447 nm (■); macroscopic viscosity (◇); (b) PEO 450000, probe size 32 nm (□); macroscopic viscosity (◆); and (c) PEO 112300, probe size 32 nm (□); macroscopic viscosity (◆)

concentrations used and the relative viscosity is plotted as S_0/S_s. The value of ρ_p, taken as 1.05, is not expected to vary with PEO concentration since the work reported applies to the adsorption plateau region, but it will differ from the density of the bare particles. Strictly, a correction term is required, but since this will not vary with PEO concentration and is difficult to quantify it has been ignored here. The value of S_0 was determined by extrapolating the sedimentation data to zero polymer concentration and therefore corresponds to the value for the particle with an adsorbed layer of polymer (or Triton) in pure water rather than the bare particle. Charge effects are not entirely absent, but in other experiments on viscosity it was shown that they merely introduce a small error (<10%) in the constant S_0 value assumed.

Figure 1 shows the microscopic relative viscosities plotted as a function of concentration for a range of probe sizes and molecular weights when no Triton is present. The measured relative macroscopic viscosity of the polymer solution, η_m, as determined in the Ostwald viscometer, is also plotted for comparison. It is clear that the microscopic viscosity calculated from the sedimentation coefficient, η_c, is greater than the experimentally measured η_m for all particle sizes and polymer molecular weights studied.

In order to show the deviations from Stokes–Einstein behaviour more clearly, *Figure 2* shows these results as plots of η_c/η_m. (This data has been generated by computer fitting the data for η_c and η_m to second order polynomials,

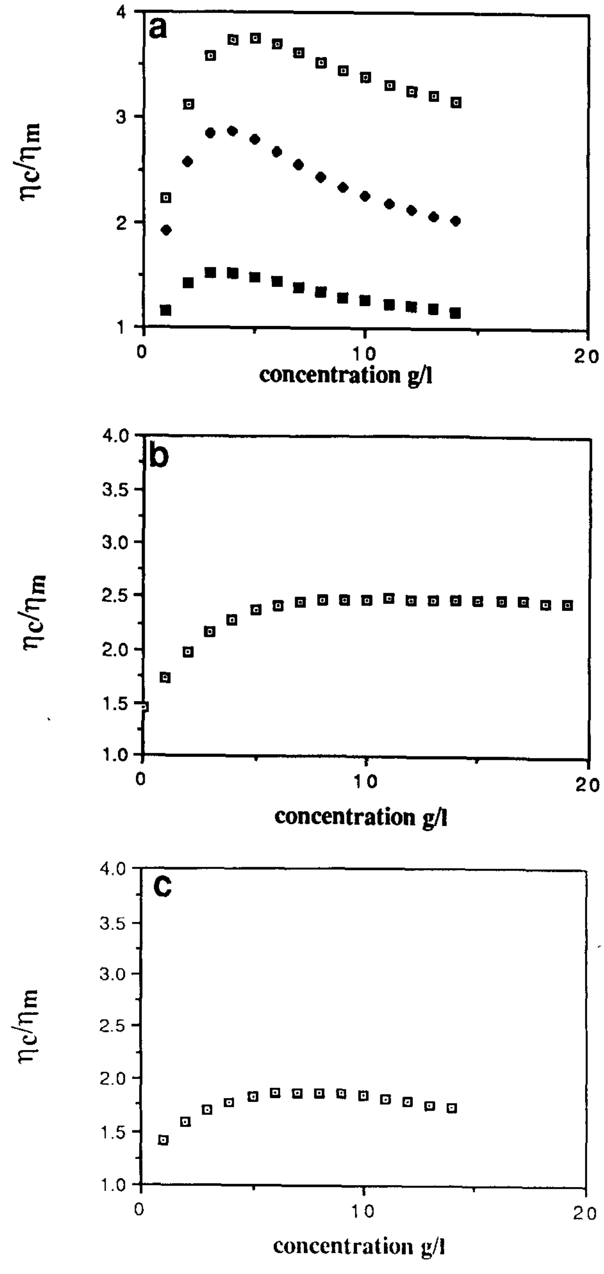

Figure 2 Deviations from Stokes–Einstein behaviour, plotted as the ratio η_c/η_m for (a) PEO 615000 with probe sizes of 32 (□), 65 (◆) and 447 nm (■); (b) PEO 450000, probe size 32 nm and (c) PEO 112300, probe size 32 nm

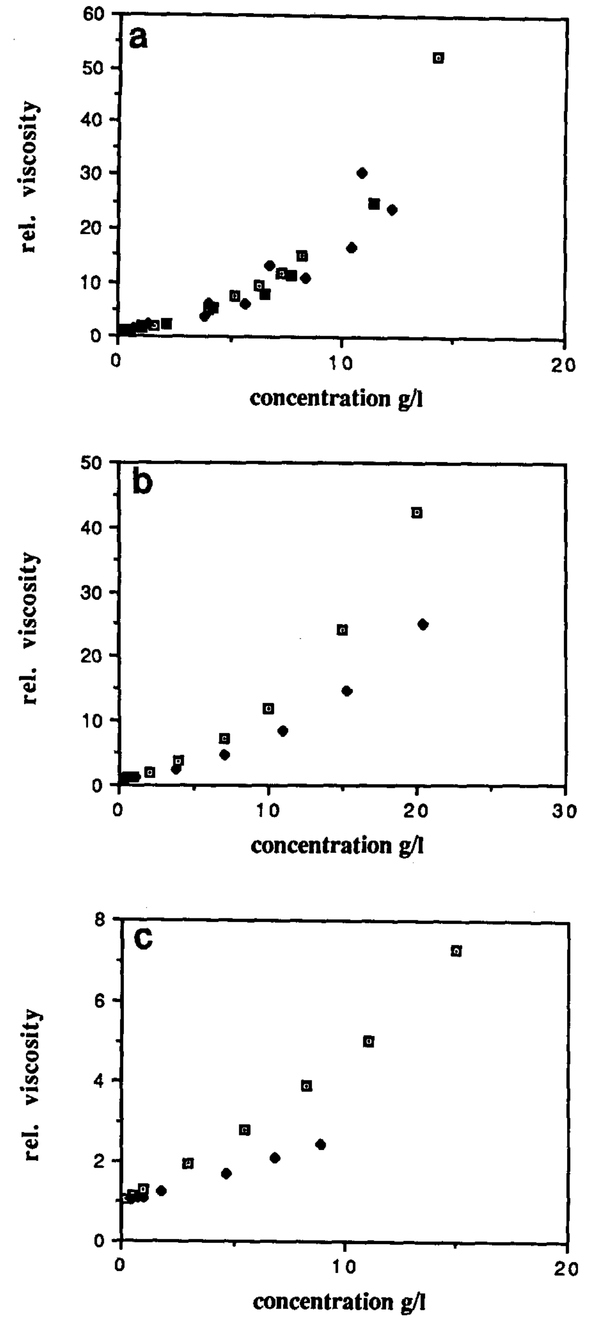

Figure 3 Comparison of the experimentally determined macroscopic and microscopic relative viscosities in the presence of 0.01% Triton in (a) PEO 615000 with probe sizes of 32 (□), 65 (◆) and 447 nm (■); macroscopic viscosity (◆); (b) PEO 450000, probe size 32 nm (□); macroscopic viscosity (◆); and (c) PEO 112300, probe size 32 nm (□); macroscopic viscosity (◆)

and then taking the ratio of these fitted curves, to smooth out experimental scatter.) For PEO 615000 (*Figure 2a*), plots for each of the three particles show a maximum at a concentration close to but slightly above C^*, followed by a gradual fall-off. The peak position is at a slightly higher polymer concentration for the smallest particle compared with the other two. Deviations from Stokes–Einstein behaviour for the 32 nm particle are very marked, with the ratio η_c/η_m reaching a value of >3.5 at its peak. The 65 nm probe particle has a maximum value for this ratio of just under three, while the large particle exhibits much less extreme behaviour, its peak ratio being only just over 1.5. It can be seen that the 32 nm particles show much greater deviations from Stokes–Einstein behaviour in the case of PEO 615000 than in PEO 112300 or 450000, although the basic shape of the graphs is similar. The peak in the curve for the PEO 112300 also seems to lie close to C^*, but for PEO 450000 the peak is not very pronounced and, if it occurs at all, it lies considerably above C^*. The reason for this rather unclear peak for this molecular weight is not obvious.

The behaviour of the probe particles was significantly different in the presence of 0.01% Triton X-100. η_c was still found to be greater than η_m (*Figure 3*) over the range of concentrations studied for all the particles and molecular weights, but the difference was much less pronounced than in the absence of Triton (cf. *Figures 1* and *3*). The effect is most marked for the highest PEO molecular weight. *Figure 4* shows the data presented as the ratio η_c/η_m. The PEO 615000 with the medium probe particles still shows a peak, but this now occurs at a value of η_c/η_m of only 1.7, compared with ~ 2.9 in the absence of Triton. The other two probe particles no longer show a peak; the ratio for the 32 nm particles is still rising at the highest concentration studied but the ratio for the 447 nm particle seems to be flattening off to a value of ~ 1.2. It is thought that the initial decrease in the value of η_c/η_m for the smallest particles simply reflects experimental scatter. For the two lower molecular weights, the ratio η_c/η_m is still rising at the highest polymer concentration examined but again for both the ratio is significantly lower than that shown in *Figure 2* when no Triton is present.

DISCUSSION

It is known[20] that when PEO adsorbs onto particles such as PS spheres, it does so with long tails extending into the solution. These tails increase in length with polymer molecular weight. We may speculate about the behaviour in the absence of Triton as follows. As the concentration is raised towards C^*, the coated particles become increasingly impeded in their motion, since the tails can interfere with the chains in solution, even though complete coil overlap to form a continuous mesh has not yet been achieved. Over the range of concentrations studied here, this interference is significant even at the lowest concentrations, since η_c/η_m is never <1. One might expect, as discussed in the Introduction, that small particles should on the contrary experience a microviscosity close to that of the pure solvent, leading to η_c/η_m being <1. However if the adsorbed tails become entangled with chains in solution, even though the unadsorbed chains are themselves not entangled with each other, locally the viscosity must increase; the adsorbed layer is effectively increasing the local chain concentration. Thus the microviscosity in this case will exceed the macroscopic as observed.

As C increases beyond C^*, first the mesh becomes complete and then the mean value of ξ decreases in accordance with equation (2). It is clear that ultimately, for high enough concentrations, the probe particle must see a continuum and the viscosity experienced by the probe particle must become similar if not identical (due to the definition of S_0 as corresponding to particles with an adsorbed polymer layer) to that measured macroscopically. The downturn apparent in *Figure 2* must

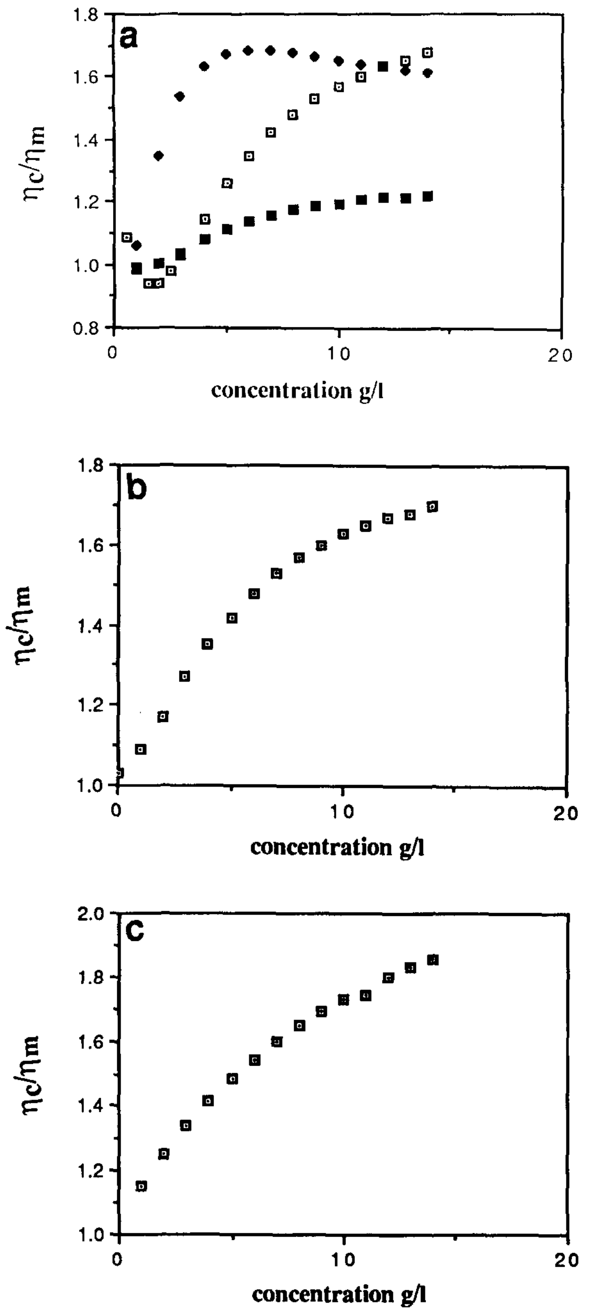

Figure 4 Deviations from Stokes–Einstein behaviour in the presence of 0.01% Triton plotted as the ratio η_c/η_m for (a) PEO 615000 with probe sizes of 32 (□), 65 (◆) and 447 nm (■); (b) PEO 450000, probe size 32 nm; and (c) PEO 112300, probe size 32 nm

correspond to the initial steps in that direction, with η_c/η_m tending towards unity.

It is difficult to predict absolutely where the peak position will occur. As the bulk chain concentration increases, the difference between the local concentration due to the adsorbed layer and the bulk value will decrease, until ultimately the bulk concentration exceeds that in the adsorbed layer. However, the adsorbed layer density itself may increase due to the osmotic compressibility of the tails (which will decrease the effective size of the probe particle). This can occur without any change in the adsorbed amount. Within this framework, one would expect a maximum difference between macroscopic and microscopic viscosities around C^*, since this is the regime where the adsorbed layer will most be modifying the particle's motion, and so the similarity in general shape for the curves of *Figure 2* is not surprising. Since the thickness of the adsorbed layer is considerably larger than the radius of the smallest particles (and correspondingly the adsorbed layer is of more importance for these particles than for the larger ones), that the η_c/η_m ratio is greatest for these small particles is to be expected. However, it is not clear that the thickness of the adsorbed layer of PEO 615000 for the 32 nm particle will necessarily reach the 96 nm quoted by Cohen-Stuart *et al.*[17] since steric hindrance due to the small radius of curvature will probably become important; thus precise quantification is not possible. Changes in the local packing of the adsorbed layer on the smallest particles due to this effect may be leading to the shift in peak position for the smallest particles in the PEO 615000, relative to the larger two particles.

Turning now to the case where Triton is present, it is clear from a comparison of *Figures 2* and *4* that the adsorption of Triton leads to a marked decrease in the deviations from Stokes–Einstein behaviour. This is demonstrated even more clearly in *Figure 5* where the η_c/η_m ratios for the 32 nm particles in PEO 615000 with and without Triton are plotted on the same graph. (The other comparative curves for different particle sizes or molecular weights are broadly similar but less marked.) However it is also clear that the sense of the deviation is still such as to retard the particle's motion, so that the appropriate viscosity is never closer to the η_s than η_m. Considering first the highest molecular weight PEO for the largest particles, although there is a significant increase above 1 in the ratio η_c/η_m in *Figure 4*, the deviation is smaller than those shown in *Figure 2*. For the PS65, the shape of the curve is very similar to that in *Figure 2*, with a peak above C^* but at a concentration somewhat higher than that observed in the absence of Triton. However the smallest particles do not seem to have reached a maximum resistance to their motion even at the highest concentrations used.

This behaviour is surprising if the Triton is completely suppressing all adsorption. However, it must be recognized that if some limited adsorption of the PEO has occurred, then the framework to discuss these results will be similar to the case discussed above when no Triton is present. In this context it should be noted that the deviations presented in *Figure 4a* are in the opposite sense to those reported by Ullmann *et al.*[13,14]. The highest molecular

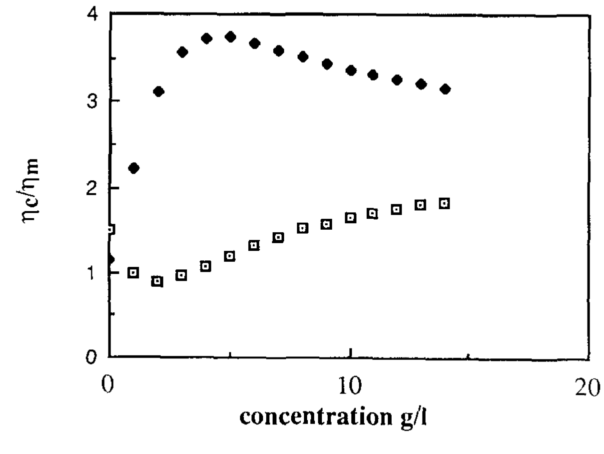

Figure 5 Comparison of η_c/η_m for 32 nm particles in PEO 615000 in the presence (□) and absence (◆) of Triton

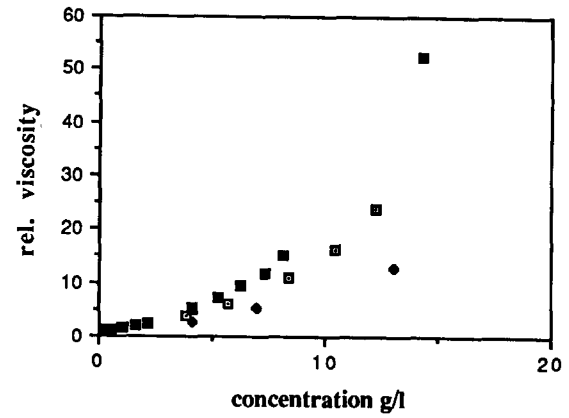

Figure 6 Comparison of the macroscopically measured relative viscosities of PEO 615000 with 0% (□), 0.01% (■) and 0.1% (◆) added Triton X-100

weight of PEO that they used was 300000, and for this all the PS probe particles (with sizes ranging from 21 to 322 nm) moved faster when Triton was present in solution (i.e. η_c/η_m, or in their notation K, was <1) than when it was not. On the other hand, we find an increased calculated viscosity corresponding to a slowing down of the probes, even when $C<C^*$. Using a molecular weight of 100000, Ullmann *et al.* did find that the smallest particles (of 21 and 52 nm radius) showed a slight rise in the η_c/η_m ratio above 1 to a value of $\leqslant 1.1$; this value remaining approximately constant for PEO concentrations in the range 10–50 g l^{-1}. Thus the magnitude of the discrepancy between η_c and η_m they measured, although now in the same sense as in our case, is seen to be significantly less than that shown in *Figure 4b* for a comparable molecular weight and probe radius.

Two possible explanations for these apparent discrepancies can be put forward, both of which may be contributing. First, the concentration of Triton used in the earlier work (0.1%) was a factor of 10 higher than in this study (0.01%). Measurement of η_m of PEO solutions when Triton is present at the higher level are plotted in *Figure 6*, together with data in the absence of Triton and with 0.01%. It can be seen that the presence of 0.01% Triton appears to cause a slightly increased viscosity, whereas 0.1% significantly reduces the viscosity. It therefore seems that even a relatively modest level of Triton of only 0.1% can interact with the PEO in some way, perhaps as a 'lubricant', reducing the polymer viscosity possibly by reducing the number of entanglements and disrupting the mesh structure. Using the higher level of 0.1% Triton for the 32 nm PS particles in PEO 615000, we are able to reproduce the finding that the microviscosity value is lower than the macroscopic in the absence of Triton (*Figure 7*).

The second possible explanation is that a level of Triton of 0.01% is too low to succeed in suppressing the adsorption of PEO chains completely. Some small number of tails may be present, which can then have a significant effect on the particle's motion, in just the same way (albeit less markedly) as when a much larger number of PEO molecules are adsorbed. This explanation can also explain why the trend of speeding up observed by Ullmann *et al.*[13] was reversed when they used low molecular weight PEO, since this would be expected to compete more effectively with the Triton for adsorption sites on the PS particles, giving rise to the existence of a few tails. Similarly in this study the ratio η_c/η_m is actually greatest (although not by much) for the lowest molecular weight studied, even though C^* is barely reached at the highest concentration investigated. However the limited data we have for the case of PEO 615000 with 0.1% Triton suggests the particles are still being slightly slowed down ($\eta_c/\eta_m \sim 1.1$).

In view of the theoretical predictions and earlier experimental work[2,7,13,14], we have attempted to fit our data to a stretched exponential of the form

$$\frac{S}{S_o} = \exp(-AC^{\nu}R^{\delta}) \qquad (4)$$

where A is a constant, C refers to the concentration of polymer and δ is assumed to be zero[11,18]. A plot of lnln (S_o/S_s) against ln (C/C^*) for the 32 nm particles in the absence of Triton shows significant scatter at low concentrations (*Figure 8a*). That the exponential fit in the absence of Triton is better at higher concentrations is consistent with the earlier discussion concerning the deviations from Stokes–Einstein behaviour being less marked at high concentrations, and supports the idea that the tails become progressively less important as the concentration is raised.

A somewhat better fit to a straight line plot is obtained for the data in the presence of Triton (*Figure 8b*), although there is still some scatter at low concentrations. By plotting in terms of the reduced variable C/C^*, it is clear from both *Figures 8a* and *b* that scaling law behaviour is obeyed, in the sense that data for PS32 for all three molecular weights cluster about the same straight line. From these plots, values of the parameter ν can be determined, although the precise value is sensitive to the concentration range considered. In the absence of Triton the ν values cluster around a value of 0.5, which is in agreement with the predictions of Cukier[21], but are lower than the value of 0.62 reported by Langevin and Rondelez[7] for PS particles in PEO without added Triton. With Triton present, when the law seems to be more closely obeyed, the values for ν are significantly higher with an average for the three molecular weights of 0.92. Thus the observed ν is higher than the values predicted by Cukier[21] of 0.5 and the de Gennes–Pincus–Velasco model prediction[3] of 0.75. However, for polyelectrolytes, Phillies and co-workers have found a

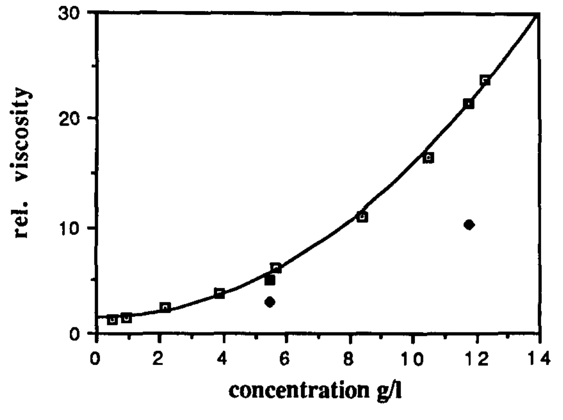

Figure 7 Comparison of the microscopic relative viscosity experienced by the 32 nm probes in PEO 615000 in the presence of 0.01% (■) and 0.1% (◆) added Triton with the macroscopically measured viscosity (□) (solid line is fitted curve as a guide to the eye)

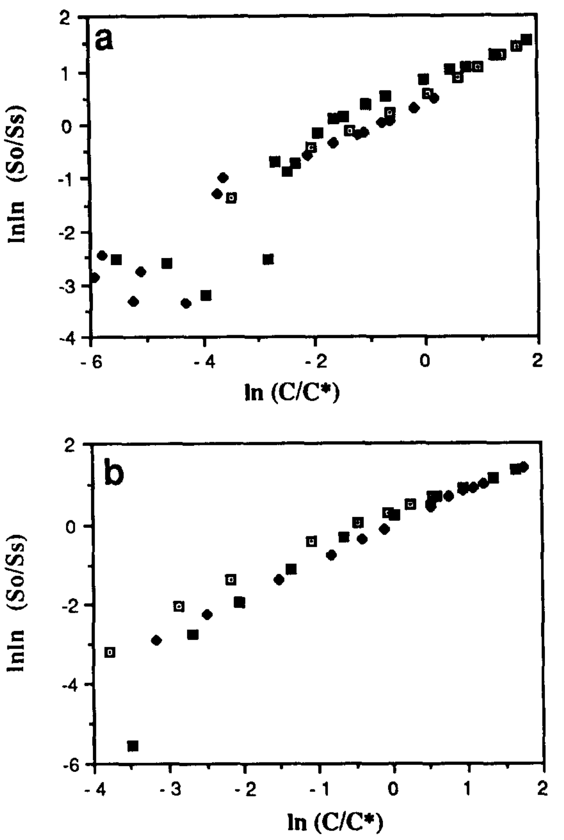

Figure 8 Plot of lnln (S_0/S_s) *versus* ln (C/C^*) for 32 nm particles (a) in the absence of Triton for PEO 615000 (■), PEO 450000 (◻) and PEO 112300 (◆); and (b) in the presence of Triton for PEO 615000 (◆), PEO 450000 (■) and PEO 112300 (◻)

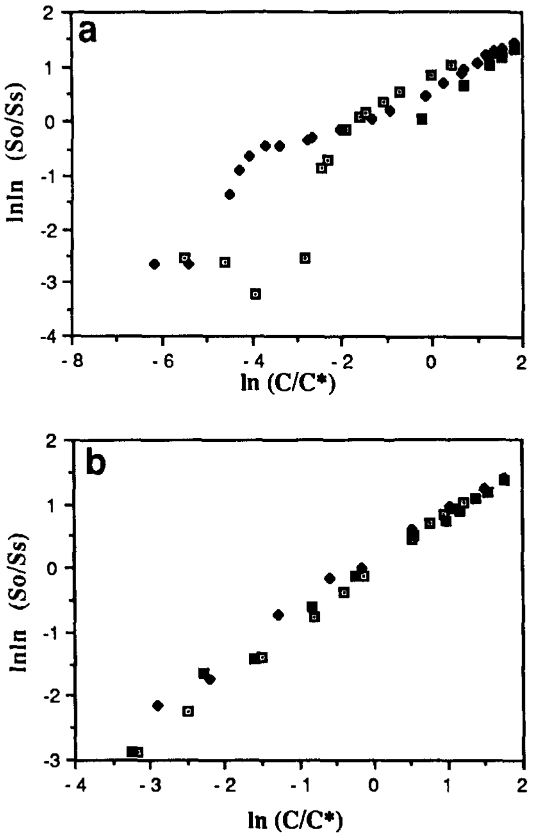

Figure 9 Plot of lnln (S_0/S_s) *versus* ln (C/C^*) (a) in the absence of Triton for PEO 615000 for the 32 nm (◻), 65 nm (◆) and 447 nm (■) probes; and (b) in the presence of Triton for PEO 615000 for the 32 nm (◻), 65 nm (◆) and 447 nm (■) probes

range of values for v between 0.5 and 1, depending on ionic strength[11]. *Figures 9a* and *b* show similar data for the three different particle sizes in PEO 615000. In this case the values for v in the absence of Triton again lie close to 0.5, but the average for the three particles in the presence of Triton is higher at 0.83.

CONCLUSIONS

The sedimentation behaviour of PS latex probes through PEO solutions has been studied for a range of probe sizes. Deviations from Stokes–Einstein behaviour, in the sense of more rapid sedimentation than expected from η_m, were observed in all cases, the deviations being greatest for the smallest particles. Such positive deviations were observed in all cases (with and without Triton), in contrast to the findings of Ullmann *et al.*[13,14] who observed negative deviations at a higher concentration of Triton. From an estimate of the value of ξ at which the resistance to motion is a maximum, some quantification of the range of pore sizes that must be present can be attempted in the case of the Triton containing solutions, when PEO adsorption is reduced. When Triton is not present uncertainty in the effective probe diameter due to the long PEO tails makes such a calculation impossible. In this case it seems that the presence of the adsorbed PEO layer can lead to an effective increase in the local PEO concentration so that the particle experiences an increase in viscosity compared with the bulk solution viscosity. The data for the Triton solutions can be fitted well to a stretched exponential of the form $S/S_0 = \exp(-AC^vR^\delta)$ with v values close to but above those predicted theoretically.

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Note added in proof

Further experiments have been carried out on the effect of varying levels of Triton addition. We believe there is an error in the macroscopic viscosity measurements when 0.1% Triton is present, as shown in *Figure 6*, and that the value of η_m is not significantly lower when Triton is present at this level; if anything it is higher. Recalculating η_c/η_m for the case of 0.1% Triton now reproduces the results of Ullmann *et al.*[13,14] that the particles are speeded up, i.e. $\eta_c/\eta_m < 1$. This result supports the view that at concentrations of Triton of 0.01% adsorption is incompletely suppressed, and that it is the tails in the adsorbed layer that are playing a crucial role. A full description of these experiments will be published separately.