Sedimentation of large colloidal particles through semidilute polymer solutions

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The sedimentation of various spherical particles with radii 25–175 Å in poly(ethylene oxide) aqueous polymer solutions have been investigated by analytical ultracentrifugation. As already observed by Laurent and Pietruszkiewicz (*Biochim. Biophys. Acta* 1961, **49**, 258) the decrease in the sedimentation rate with polymer concentration, c, and particle radius, R, is of the form $S \propto \exp(-Ac^{\nu})$. Present experiments in semidilute solutions show that: (1) A is proportional to R but independent of polymer molecular weight; (2) ν is $\simeq 0.62$, significantly higher than the value of 0.5 claimed by previous authors; (3) polymer adsorption onto the particle surfaces has to be taken into account. Our results are in reasonable agreement with a simple form $S \propto \exp(-R/\xi)$ where ξ is the correlation length $\propto c^{-\nu}$ with $\nu \leqslant 0.75$. The semidilute polymer solution can thus be viewed as a statistical network of mesh ξ, the retardation factor being governed by the elastic distortion of the network due to the moving particles.

INTRODUCTION

The present paper is concerned with ternary mixtures polymer/solvent/colloidal particles of radius R (10–1000 Å). We are interested here in the mobility of the particles as measured by sedimentation experiments.

If the radius, R, of the particle is very small, it experiences a friction coefficient $f_0 = 6\pi\eta_0 R$, where η_0 is the solvent viscosity. But if R is very large, we expect the friction coefficient to be much greater, $f = 6\pi\eta_M R$, where η_M is a macroscopic viscosity coefficient which can be several orders of magnitude higher than η_0.

Recently, theoretical arguments[1,2] have considerably helped in making this picture more quantitative. Above a given concentration, c^*, the polymer chains begin to entangle. The solution is said to be semidilute. It is possible to define a characteristic correlation length $\xi(c)$, dependent on concentration but independent of the molecular weight M. ξ describes the average distance between entanglement points at a given monomer concentration. $\xi \propto c^{-3/4}$ for neutral polymer[3], $\xi \propto c^{-1/2}$ for polyelectrolytes[4].

In the semidilute regime, the polymer solution can be viewed as a transient statistical network of mesh ξ. Under these conditions, it becomes clear than the frictional force experienced by a particle of radius R will be totally different according to whether R is greater or smaller than ξ. In the semidilute regime, de Gennes, Pincus and Velasco[5] have argued for the existence of a scaling law:

$$f_0/f_c = \psi(R/\xi)$$

where f_c is the friction coefficient at concentration c. The detailed form of ψ is not predicted, but it was expected that $\psi(x) \sim 1$ for $x < 1$ and $\psi(x) \sim \eta_0/\eta_M$ for $x \gg 1$, where η_M is the macroscopic viscosity of the solution.

At that time, the experimental situation was not totally clear and did not allow for an easy comparison with the theoretical predictions, despite numerous experimental results by Laurent and coworkers[6–8] in concentrated polymer solutions and Morris and Morris in polyacrylamide gels[9]. A recent experiment by Donners is also worth mentioning[10].

All authors have pointed out a striking variation of the friction coefficient with particle radius and polymer concentration. They propose an empirical expression of the form:

$$f/f_0 \propto \exp(Rc^{1/2})$$

for polymer solutions, (neutral polymers and polyelectrolytes with salts)[6–8,10] and for gels[9]:

$$f/f_0 \propto \exp(R^2c)$$

However the results were not molecular weight independent, contrary to theoretical expectations.

In view of this situation, it seemed important to start new experiments on carefully controlled (molecular weight, polydispersity) neutral polymer solutions whose properties are at present much better understood than those of polyelectrolytes or gels. In this paper, we present a systematic study of the sedimentation coefficients of various spherical particles (ludox, bovine serum albumin, viruses) in semidilute solutions of poly(ethylene oxide) in water. It will be shown that coherent results can indeed be obtained if the absorption of polymer chains onto the sedimenting particles is taken into account.

In this paper, we first describe the materials and the techniques chosen to perform the measurements. We present the results of our sedimentation studies and point out the importance of using monodisperse polymers and the effect of varying the concentration of the diffusing particles. We show that our data, although qualitatively similar to those previously obtained, are in better agreement with the theoretical predictions. We emphasize the necessity of correcting for the polymer adsorption onto the particles. Finally

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we discuss the adsorption properties for our solutions as extracted from our experimental data (adsorption layer thickness, adsorption isotherm).

EXPERIMENTAL

Materials

Most of the known colloidal particles are soluble in water and insoluble in organic solvents. It was therefore necessary to chose a water-soluble polymer. Among several neutral water-soluble polymers, poly(ethylene oxide) (PEO) was selected, since it has been extensively described in literature. PEO of various molecular weights is available commercially from Union Carbide: 'Polyox' WSR 301 ($M = 4 \times 10^6$) and WSR 205 ($M = 6 \times 10^5$). However, it became apparent from our results that these materials are poorly defined. More reliable data have been obtained with anionic PEO synthesized by Deffieux and Boileau[11] of molecular weights 337 000, 300 000 and 140 000. The polymer concentrations were chosen to be larger than c^*. Earlier measurements[12] have shown that $c^* = 5 \times 10^{-4}$ g/cm^3 for $M = 140\,000$; $c^* = 3 \times 10^{-4}$ g/cm^3 for $M = 300\,000$; and $c^* = 2 \times 10^{-4}$ g/cm^3 for $M = 600\,000$.

Particles studied were a globular protein (bovine serum albumin, $R = 25$ Å) obtained from Sigma Chemicals, colloidal silica 'Ludox HS 30' ($R = 70$ Å), which is a light scattering standard from Dupont Chemicals, egg plant mosaic virus (EMV, $R = 150$ Å), tomato bushy stunt virus (TBSV, $R = 175$ Å), and polystyrene latex spheres ($R = 460$ Å) from Dow Diagnostics.

Samples were prepared by dissolving the polymer in aqueous solutions containing the particles and stirring for 24 h to ensure equilibrium before use. In the case of commercial polymers we found it necessary first to disperse the polymer into a non-solvent, such as isopropanol, to ensure good dilution[13]. The solvent was pure tridistilled water, except for proteins and viruses for which we used a phosphate buffer (KCl 2 M, KH_2PO_4 2 mM, K_2HPO_4 8 mM).

We found it extremely difficult to dissolve PEO in polystyrene latex solutions. In most cases, one of the components precipitated and no satisfactory results were obtained with this system.

Methods

The aim of this study was to measure the frictional force experienced by the particle in the polymer solution. Several physical properties are directly related to f (ref 14): the diffusion coefficient $D = kT/f$; the sedimentation coefficient $s = m(1 - \rho_0/\rho)/f$, (where m is the particle mass, ρ is the particle density and ρ_0 is the solvent density); the electrophoretic mobility, etc.

The measurement of the sedimentation coefficient s turned out to be the most convenient method. We used a commercial analytical ultracentrifuge, Beckman Spinco model E. Top speed was 60 000 rpm, with a sample cell placed 6.5 cm from the centre of rotation. Maximum acceleration was 250 000 g and caused the particles to sediment towards the bottom of the cell.

Let us consider first a single particle species in a uniform solvent[14]. The centrifugal force per particle is $m\omega^2 r$, where ω is the angular velocity of the rotor and r the distance from the centre of rotation. Countering this force is the buoyancy force exerted by the solvent:

$$m\rho_0\omega^2 r/\rho$$

The net force per particle is thus:

$$F = \omega^2 rm(1 - \rho_0/\rho)$$

In the steady state regime, F will impart a constant velocity to each particle: $v = F/f$. The flow velocity, v, like the sedimenting force, depends on rotor speed and on the distance r from the centre of rotation. It is therefore convenient to define a new quantity, the sedimentation coefficient, s:

$$s = \frac{v}{\omega^2 r} = \frac{m}{f}(1 - \rho_0/\rho) \tag{1}$$

which depends only on molecular parameters, and is constant with respect to time. If the particles are identical they will sediment with the same velocity. A sharp boundary will be formed at the position r_h between the region where only solvent is present ($r < r_h$) and the region containing both solvent and particles ($r > r_h$). The boundary will move with velocity v, so that s can be determined from the time variation of r_h. Experimentally, a schlieren optical system provides the shape of the refractive index gradient dn/dr in the cell and r_h is the position at which dn/dr is a maximum.

One advantage of the ultracentrifugation technique is that the motion of particles can easily be separated from that of the polymer when polymer and solvent densities are close. In that case, the sedimentation rate of the polymer can be neglected, and we are left with sedimentation of one kind of particles through a uniform polymer/solvent solution at rest.

In the other case where the sedimentation coefficient of the particles and the polymer are not very different (e.g. with particles of small radius), it is necessary to correct for the polymer motion relative to the solvent and to the particles. We have adopted a very simple model in which we consider that the frictional force on the particle is the sum of the frictional force exerted by the solvent and the friction exerted by the polymer chains:

$$F = f_0 v + f_p(v - v_p) = f_e v \tag{2}$$

where v is the velocity of the particle with respect to the solvent; v_p is the velocity of the polymer; f_0 and f_p are the frictional coefficients exerted by the solvent and the polymer on the particle; f_e is the measured effective friction coefficient, $f_e = s/m(1 - \rho/\rho_0)$.

We are interested in the value of the friction coefficient f in a situation where both solvent and polymer are at rest, i.e. $v_p = 0$. In this case equation (2) becomes:

$$F = f_0 v + f_p v = fv$$

The value of f is related to the measured sedimentation coefficients s_0, s and s_p through the relation:

$$f = f_0\frac{s_0 - s_p}{s - s_p} \tag{3}$$

where s_0 is the sedimentation coefficient of the particle alone, s_p that of the polymer alone and s that of the protein in the polymer solution.

If s_p is very small compared with s_0 and s, then we obtain

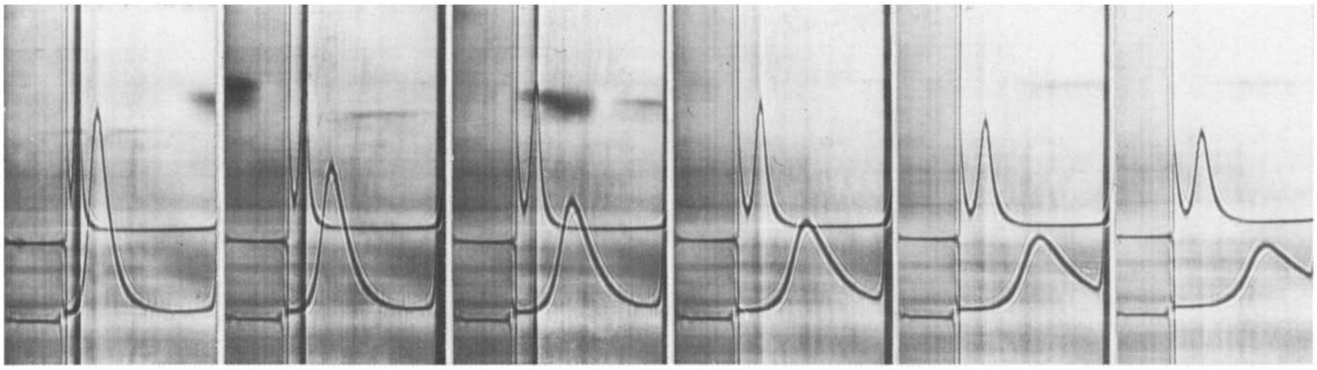

Figure 1 Typical sedimentation pattern obtained with ludox particles in pure water (bottom 6 curves) and in a 10^{-2} g/cm^3 PEO polymer solution (top 6 curves). Time between exposures, 4 sec; rotor speed 30 000 rpm

the classical result:

$$f \simeq f_0 s_0 / s$$

RESULTS

All measurements were made at 20°C. Different rotor speeds were used between 20 000 and 60 000 rpm and gave identical results.

Ludox solutions

Dilute ludox solutions were used for calibration purposes. In *Figure 1* a typical sedimentation pattern obtained with the analytical ultracentrifuge is shown. The lower trace corresponds to a 1% by wt ludox solution. The time interval between the exposures was 4 sec, the cell length was 1.36 cm and the rotor speed was 30 000 rpm. The sedimentation coefficient of ludox in water, for samples from two different batches, was found to be:

$$s^0_{20w} = (120 \pm 10)\ \mathrm{S}$$

$$s^0_{20w} = (135 \pm 10)\ \mathrm{S}$$

where S stands for the standard Svedberg unit = 10^{-13} sec. Taking the density of ludox particles to be $\rho = 2.279$ (ref 15), we calculate from equation (1) radii in reasonable agreement with the average value of 77 Å given by the manufacturer[15]: $R_1 = 65$ Å; $R_2 = 69$ Å.

PEO solutions

The values of the sedimentation coefficient s_p of the PEO polymer in aqueous solutions are given in *Figure 2* as a function of polymer concentration c. s_p values are much smaller than those obtained for ludox particles. s_p varies between 1 S and 0.2 S typically and does not seem to depend on the polymer molecular weight in the semidilute regime ($c > c^*$). For $M = 300\,000$ and $140\,000$, $s_p(c)$ follows a simple power law dependence:

$$s_p \propto c^{-0.4 \pm 0.1}$$

This result is in rough agreement with theoretical predictions based on dynamical scaling[16] which state:

$$s_p \propto \frac{c\xi^2}{\eta_0} \propto c^{-0.50}$$

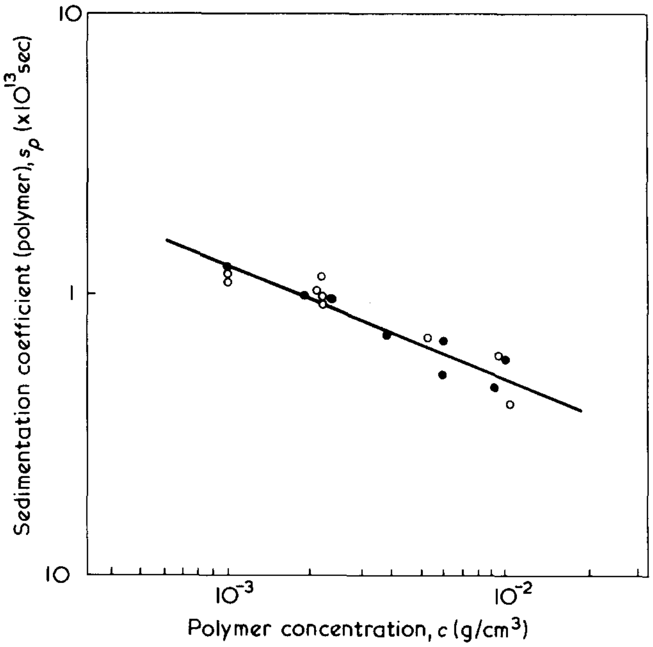

Figure 2 Sedimentation rate of PEO polymer chains, s_p, *versus* polymer concentration c in aqueous solution, log–log plot. The straight line corresponds to the best fit $s_p \propto c^{-0.4}$. Slope of line, 0.4. ○, M = 140 000; ●, M = 300 000

Ludox–PEO polymer solutions

Polydisperse PEO. Measurements were made on commercial WSR 301 ($M_w = 4 \times 10^6$), WSR 205 ($M_w = 600\,000$) and a sample of mass 250 000 obtained by fractionation of the WSR 205. The polymer concentration range was typically $5 \times 10^{-4} < c < 10^{-2}$ g/cm^3, larger than c^* for all the molecular weights studied.

Figure 1 illustrates the difference between sedimentation velocities of ludox in pure water (lower trace) and in a polymer–water solution (upper trace). It is clear that the ludox particles move much more slowly when PEO is added to the solution. *Figure 3* shows the dependence of the sedimentation coefficient, s, for ludox *versus* polymer concentration c. Ludox concentration was about 1%. s decreases steadily from 120 down to 3 S. However, s values are widely dispersed. We have attributed this dispersion to difficulties in the dissolution of these poorly defined macromolecular chains (chain branching). Indeed, scattering of the data points was even larger when the polymer was added to water directly, without predispersion.

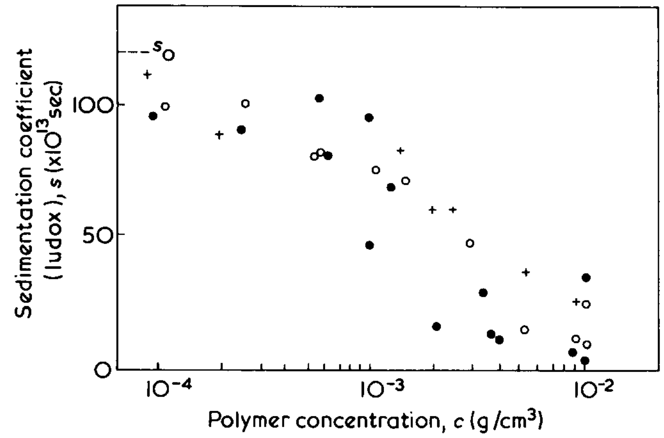

Figure 3 Sedimentation rate of ludox in PEO polymer solutions (commercial PEO, M = 250 000, 600 000 and 4 x 10^6); ludox concentration = 10^{-2} g/cm^3. ●, WSR 301; ○, WSR 205; +, fraction M = 250 000

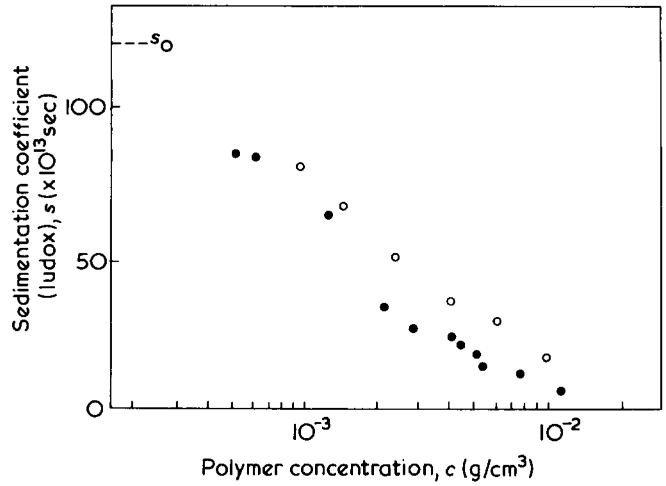

Figure 4 Sedimentation rate of ludox in PEO polymer solutions (anionic PEO, M = 140 000 and 300 000); ludox concentration = 10^{-2} g/cm^3 ●, M = 300 000; ○, M = 140 000

Monodisperse PEO. Poly(ethylene oxide), prepared by anionic polymerization, had a much sharper mass distribution than commercial PEO, typically $M_w/M_n \lesssim 1.1$. In addition, it was observed to dissolve more easily in water.

The results for the sedimentation coefficients, s, of ludox in the monodisperse polymer–water solutions are given in *Figure 4*. The ludox concentration was 1%. The results are qualitatively similar to those of *Figure 3*. However, data dispersion is now much smaller and s exhibits a clear molecular weight dependence. For a given polymer concentration c, s is larger for M = 300 000 than for 140 000, typically by a factor of 2.

The dependence of s on c has been plotted in *Figure 5* (A and B) using logarithmic scales. We obtain:

$$s/s_0 = \exp(-Ac^y)$$

with: $y = 0.67 \pm 0.07$ for M = 300 000; $y = 0.65 \pm 0.05$ for M = 140 000.

The y exponents are identical for the 2 polymer masses, within experimental accuracy. But the A values are molecular weight dependent.

The macroscopic viscosity of a 1% solution of PEO of molecular weight 337 000 was measured with a Couette viscometer at low shear (10^{-2}–1 sec^{-1}). We obtain η = 2.40 cp, in good agreement with literature data[13,17]. Thus $\eta/\eta_0 = \eta_{\text{relative}} = 2.4$. It is striking to note that at the same 1% concentration, the sedimentation factor for ludox particles has decreased by a much larger factor, from s_0 = 125 S to a retarded value of s = 6 S. Laurent and Persson[8] observed that the retarding effect is thus not directly proportional to the macroscopic viscosity of the solution. We will discuss this problem below.

Effect of ludox concentration. In solutions of pure ludox, the sedimentation coefficient depends weakly on ludox concentration, c_L. Separate experiments showed that:

$$s = s_0(1 - kc_L) \qquad (4)$$

with $k \simeq 6$ cm^3/g. This behaviour is classical for spherical particles[14]. The dependence of s on concentration c_L is much larger when PEO is added to the solution. At fixed polymer concentration c, s (c_L) no longer follows a simple linear law as in equation (4). *Figures 6* and *7* show the results obtained with two different polymer masses. For M = 337 000 and c = 1.9 x 10^{-3} g/cm^3 (see inset), s varies between 64 and 99 S for c_L = 1 x 10^{-3} up to 9 x 10^{-3} g/cm^3.

In view of these results, significant data can only be obtained if extrapolations to zero ludox concentration are made. This corresponds to the broken line in *Figures 6* and *7*. The dependence of s on c, at $c_L \to 0$, again follows a law:

$$s/s_0 = \exp(-Ac^y)$$

with $y = 0.62 \pm 0.10$, slightly lower than the earlier determination of $y = 0.67 \pm 0.07$ at a finite ludox concentration, c_L = 1%.

The y exponent is the same for the 2 molecular masses studied. Comparison of *Figures 6* and *7* show that the absolute s values are also identical. This means that A is now molecular weight independent.

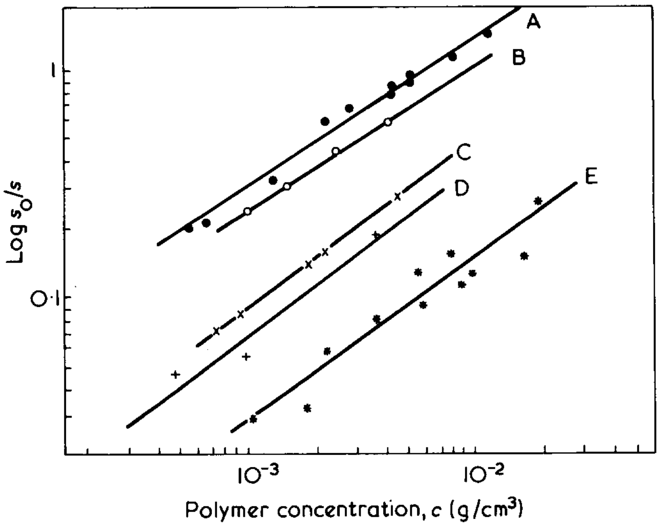

Figure 5 Log log s_0/s *versus* log c where c is the polymer concentration for various particles ludox, bovine serum albumin, TBSV and EMV viruses at finite particle concentration (see text). (PEO, M = 140 000 and 300 000). A, slope 0.67; B, slope 0.65; C, slope 0.75; D, slope 0.75; E, slope 0.70. ●, Ludox M = 300 000; ○, ludox M = 140 000; x, EMV M = 300 000; +, TBSV M = 300 000; *, BSA M = 300 000

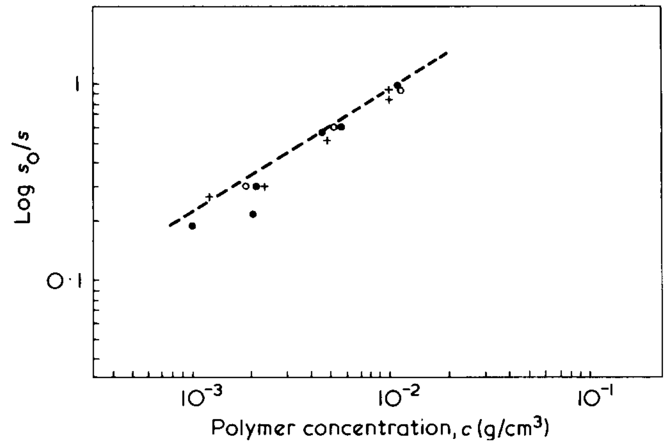

Figure 6 Log log s_0/s *versus* c the polymer concentration for ludox particles at various ludox concentrations c_L. The dotted line corresponds to the extrapolation of the data to zero ludox concentration. PEO molecular weight = 140 000. Ludox concentration: ●, 0.9–1%; ○, 0.4–0.5%; +, 0.1%

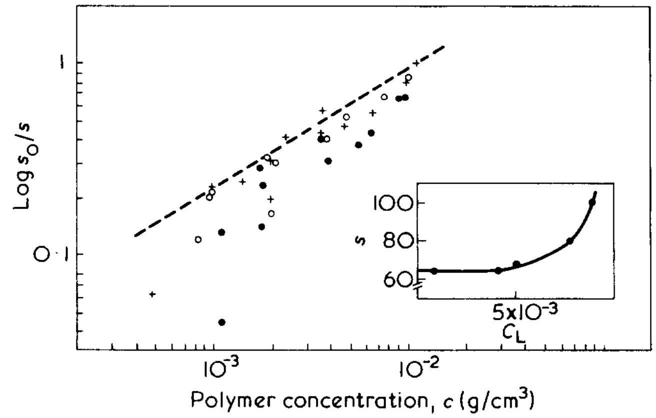

Figure 7 Same as *Figure 6* but for PEO molecular weight = 337 000. Ludox concentration: ●, 0.8–1%; ○, 0.3–0.5%; +, 0.1%. The inset shows the dependence of *s versus* ludox concentration c_L at a fixed polymer concentration $c = 1.9 \times 10^{-3}$ g/cm^3

Protein and viruses/PEO polymer solutions

The sedimentation data obtained for the BSA protein and the EMV and TBSV viruses in PEO solutions of molecular weight 300 000 are shown in *Figure 5*. They are given for finite particle concentrations: 5×10^{-3} g/cm^3 for BSA and TBSV, 3×10^{-3} g/cm^3 for EMV. In *Figure 8* we have repeated the measurements on BSA at three different particle concentrations, $c_{BSA} = 0.9 \times 10^{-4}$, 1.0×10^{-3} and 5×10^{-3} g/cm^3, to investigate the dependence of s on c_{BSA} (see inset of *Figure 8*). Plotted on logarithmic scales, the data of *Figure 5* fit the law:

$$s/s_0 = \exp(-Ac^y)$$

with $y = 0.75$ for EMV and TBSV and $y = 0.70$ for BSA.

We have already discussed, in the case of ludox particles, the problem of extrapolating the s data to zero particle concentration. In the case of BSA a second correction is necessary because its sedimentation coefficient takes low values, close to that of the polymer itself: the motion of the polymer can no longer be neglected. *Figure 9* displays a sedimentation pattern picture which shows clearly this effect. The lower trace corresponds to pure BSA and has only one peak ($s^0_{20,w} = 4.5$ S). The higher trace corresponds to BSA in a 10^{-3} g/cm^3 PEO solution and has two closely-spaced peaks. The 'fast' peak represents the boundary between regions with and without BSA. The 'slow' peak represents the boundary between pure solvent and solvent/polymer. The s values for BSA have been corrected using the procedure described above. This correction is dominant over the range of particle concentration effects.

For BSA after making all these corrections, we obtain:

$$s/s_0 = \exp(-Ac^y)$$

with

$$y = 0.52 \pm 0.20$$

The uncertainty in y is largely due to the difficulty of measuring small s values and to the imprecision on the polymer sedimentation data used to correct for the polymer motion.

No such correction was made with the two viruses after it was observed that the dependence on particle concentration is extremely rapid. In this case, the extrapolation of our data to zero particle concentration should be meaningless.

DISCUSSION

Theory

We have already mentioned in the Introduction that the retardation factor introduced on the particle motion by the presence of the polymer network should obey a scaling law:

$$s/s_0 = \psi(R/\xi)$$

One possible form for the scaling function has been quoted[5]:

$$\psi = \exp[-(R/\xi)^\delta] + \eta_0/\eta_M \tag{5}$$

This expression was obtained by estimating the reduc-

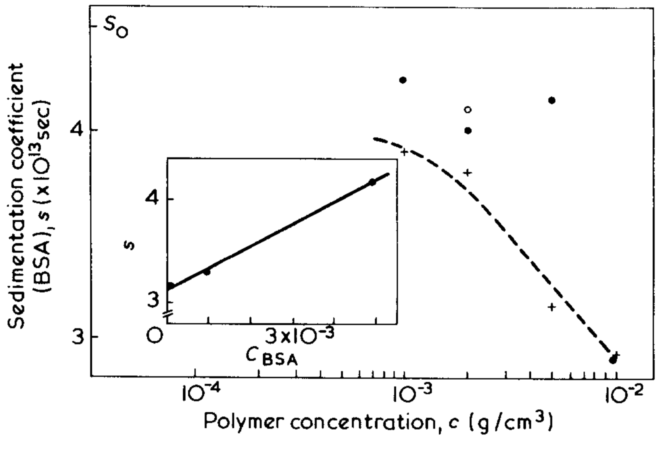

Figure 8 Sedimentation rate of BSA in PEO polymer solutions *versus* polymer concentration at various BSA concentrations. (– – – –), Corresponds to the extrapolation of data to zero BSA concentration (see inset). In this Figure, the data have not yet been corrected for polymer motion. PEO molecular weight = 140 000. BSA concentration: ●, 5%; ○, 1%; +, 0.09%; $c_{PEO} = 5 \times 10^{-3}$

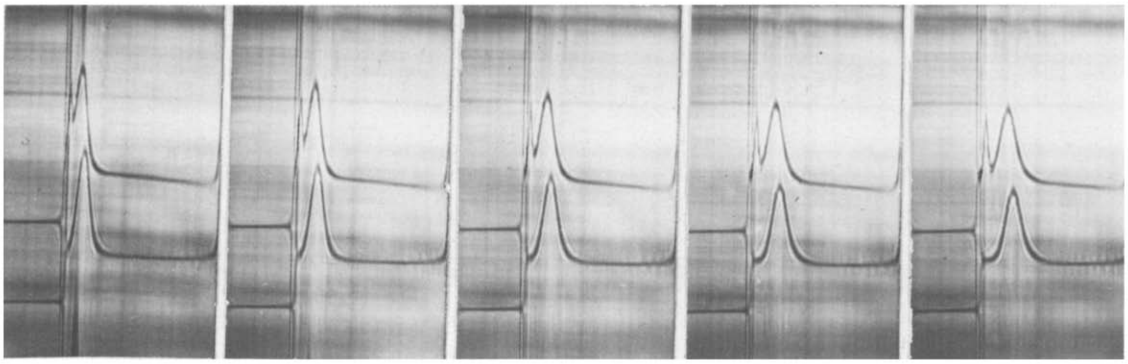

Figure 9 Typical sedimentation pattern obtained with BSA particles in pure water (bottom 5 curves) and in a 10^{-2} g/cm^3 PEO polymer solution (top 5 curves)

tion of entropy of one mesh unit (original size ξ) when it is extended to size R. In a simple picture with fixed entanglement points one would expect $\delta = 2.5$ (larger than the value for ideal chains, $\delta = 2$). In a more realistic picture in which the entanglements are not fixed, the barrier must be reduced and the exponent δ should be smaller.

Writing the dependence of the coherence length ξ on concentration for neutral polymers, $\xi \propto c^{-3/4}$, we find:

$$s/s_0 \propto \exp - (Rc^{3/4})^{\delta} \qquad (6)$$

This is a generalized version of an expression previously derived by Ogston[18] on the basis of a particular stochastic model of diffusional migration in rod systems:

$$s/s_0 \propto \exp -(Rc^{1/2}) \qquad (7)$$

Note that equation (6) predicts that s/s_0 should be independent of polymer molecular weight (as is ξ). The aim of the following discussion is to compare these assumptions with our experimental findings.

Dependence of s/s$_0$ *on polymer concentration*

The results obtained with ludox particles in monodisperse polymer solutions show:

$$s/s_0 \propto \exp(-Ac^y)$$

with $y = 0.62 \pm 0.10$ in the limit of zero particle concentration.

This exponent, although clearly greater than 0.5 is still rather far from the 0.75 value predicted by the de Gennes–Pincus–Velasco model*[5]. However the agreement is much better if we take a value of 0.67 for the theoretical exponent as derived from dynamic light scattering experiments in semidilute polystyrene solutions[19]. We have no definite explanation for the deviation of these exponents from the ideal value of 0.75. The hypothesis of complete flexibility of the polymer chains may appear inadequate for dynamic behaviour. This could explain why the PEO exponent is still lower than that for polystyrene, since PEO is known to be less flexible[17]. The results with BSA particles give $y = 0.52 \pm 0.20$. However these data are much less precise than those with ludox.

On the other hand it is remarkable that when the results of Laurent and Pietruszkiewicz[6,7] are reanalysed without supposing *a priori* the exponent to be 0.50, we obtain: $y = 0.5$ for latex particles, $R = 1825$ Å; $y = 0.75$ for latex particles, $R = 440$ Å; $y = 0.78$ for ludox particles; $y = 0.6$ for BSA particles, instead of $y = 0.5$ as claimed by these authors.

Dependence on polymer molecular weight

The theory clearly states that the retardation factor, s/s_0, should be independent of polymer molecular weight whenever $c > c^*$. It is clear from our results (see *Figures 6* and *7*) that the variation of s with polymer concentration is indeed independent of polymer molecular weight in the limit of zero diffusing particle concentration. On the contrary, when no extrapolation is made, the absolute values of s are highly dependent on molecular weight, being shifted by as much as a factor 2, for the two values of M, 140 000 and 300 000, although the y exponent stays approximately the same. This spurious molecular weight dependence was also evident in the experiments of Laurent and Pietruszkiewicz (see *Figure 5* of ref 6). Thus their experiments are only qualitatively correct.

Dependence of s/s$_0$ *on particle radius*

The necessity of using rigid spheres which are well calibrated and non-aggregated was a very stringent restriction to the number of particles which could be used. Moreover, the unreliable results obtained with the viruses and the latex spheres have forced us to restrict the analysis to the data obtained for only two different particle sizes, i.e. ludox spheres $R \simeq 70$ Å and BSA protein $R \simeq 25$ Å. Consequently, we shall not attempt to explore the R dependence of s/s_0 explicitly. We will show that the absolute values of ξ derived from the two series of experiments are entirely consistent and are also fully compatible with an independent determination of ξ.

This is done in *Table 1* where the ξ values at various polymer concentrations have been calculated using $s/s_0 = \exp(-R/\xi)$ (assuming $\delta = 1$ in equation 5). We have taken the data extrapolated to zero diffusing particle concentration for s. The error bars correspond to the uncertainty in the true particle radius. The adsorbed polymer layer thickness is estimated to be 10 Å (see below).

The last column gives a value of ξ at $c = 1\%$ as obtained on the same PEO–water system in a separate study of the

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* We assume here that $\delta = 1$, as will be justified in a later section on the R dependence of s/s_0.

Table 1 Calculated values of the correlation length ξ as a function of PEO polymer concentration c, assuming $s/s_0 = \exp(-R/\xi)$. The second and third columns correspond to two separate experiments with ludox and BSA particles, respectively. The error bars are obtained by varying the particle radius by 10 Å to account for the polymer adsorption layer thickness (PEO, M = 140 000 and 300 000). The value ξ = 31 Å is derived independently from an experimental determination of the cross over between the dilute and semidilute regimes

c (g/cm^3)	Ludox (Å)	BSA (Å)	Ref (12) (Å)
1×10^{-3}	138 (±20)	125 (±50)	
2×10^{-3}	90 (±12)	110 (±40)	
5×10^{-3}	50 (±8)	52 (±20)	
1×10^{-2}	33 (±5)	48 (±20)	45

Table 2 Calculated values of the correlation length at a 1×10^{-2} g/cm^3 PEO polymer concentration for various particles, assuming $s/s_0 = \exp(-R/\xi)$. Contrary to *Table 1*, no extrapolation to zero particle concentration has been made. Note that the ξ values are widely different

Particle			Polymer mass	s/s_0	ξ (Å) (at polymer concentration $c = 10^{-2}$ g/cm^3)
Name	Concentration (g/cc)	Radius (Å)			
Ludox	1×10^{-2}	69	140 000	0.70	30
	1×10^{-2}		300 000	0.039	22
BSA	5×10^{-3}	25	300 000	0.722	76
EMV virus	3×10^{-3}	150	300 000	0.315	130
TBSV virus	5×10^{-3}	175	300 000	0.482	240

crossover between the dilute and semidilute regimes[12]. When c is gradually increased the polymer coils begin to entangle. At $c = c^*$ the mean distance between separate coils is equal to the end to end distance of a single chain, L. As ξ is the mean distance between contact points of separate chains, we have $\xi = L/2$ at $c = c^*$. From our experiments, a c^* value of 10^{-2} g/cm^3 should correspond to polymer chains of molecular weight 3000. Taking their L values from the literature[17], we know that $\xi = L/2 \simeq 45$ Å at a concentration of 1% in PEO–water semidilute solutions. This is in excellent agreement with the value estimated from our present sedimentation experiments (*Table 1*).

Again, it should be emphasized that if the same analysis was made at finite particle concentration, the calculated ξ values at a fixed polymer concentration of 1% would be totally inconsistent between the various diffusing particles. This is shown in *Table 2* where the particle concentration used in each experiment is indicated in the second column.

We will now try to explain the necessity for extrapolating all the results to zero particle concentration.

Polymer adsorption

Adsorption of poly(ethylene oxide) from water into various solid and liquid interfaces has been widely investigated in the literature[20]. It is well known, for instance, that colloidal silica such as ludox is the substrate of choice for adsorption studies of PEO because of its high specific surface, ~200 m^2/g. Adsorption of PEO on biological surfaces as proteins and viruses is less known but also likely to be important.

For our sedimentation studies, the adsorption of some polymer chains onto the particle surfaces will have two different effects: (1) changing the effective polymer concentration in the solution and (2) increasing the particle radius by the adsorbed layer thickness. Moreover, it can be expected that the magnitude of both effects will depend on polymer molecular weight.

The change of particle radius $R = R_0 + \Delta R$ is only a second order effect. A large number of experiments have already shown that PEO usually adsorbs on silica in a very flat configuration. $\Delta R \lesssim 10$ Å[21] and thus $R \simeq R_0$. Of course, the correction is more important for small size particles such as BSA rather than for ludox. Our determination of ξ given in *Table 1* shows that changing the particle radius by 10 Å does not significantly affect the results.

Of much more importance is the change in the effective polymer concentration, c_e, in free solution. Its value can be estimated from the s_0/s results given in *Figures 6, 7* and *8*. If we take one experimental point at a given c and for a finite particle concentration, the corresponding s_0/s value falls below the dotted line which corresponds to extrapolation to zero particle concentration. This happens because c is not the true polymer concentration in the solution c_e, but rather the sum of c_e and of the adsorbed amount c_a. c_e is directly obtained from the abscissa of the broken line of same ordinate s_0/s. The adsorbed polymer concentration is then $c_a = c - c_e$. It is noticeable from the scattering of the experimental results of *Figures 6, 7* and *8* that c_a varies widely between experiments, all conditions being kept constant. It is thus not possible to deduce a significant adsorption isotherm c_a *versus* c from these data. Therefore we shall only estimate the number, N, of polymer chains adsorbed per solid particle. Results for ludox particles are given in *Table 3*. N is of the order of unity, and dependent on polymer molecular weight. $N = 1$ corresponds to $c_a = 1.2 \times 10^{-3}$ g/cm^3 for a total polymer concentration $c = 2.2 \times 10^{-3}$ g/cm^3 and a particle concentration $c_L = 10^{-2}$ g/cm^3 in the case M = 337 000.

If we now calculate the area corresponding to one monomer at the surface of the particle, we obtain:

$$A = 4\pi R^2 \frac{m}{M}$$

where m = monomer molecular weight. For M = 340 000, our results give A = 8 Å^2/monomer for one chain/particle and for M = 140 000, A = 20 Å^2/monomer (one chain/particle).

Since the area per monomer is expected to be ~20 Å^2 for a perfectly flat configuration[22] we conclude that this is

Table 3 Number, N, of polymer chains adsorbed per ludox particle *versus* free polymer concentration c_e in the solution (PEO 140 000 and 337 000)

c_e (g/cm^3)	N for M = 337 000	N for M = 140 000
1×10^{-3}	1	1
3×10^{-3}	2	1
5×10^{-3}	3	1
1×10^{-2}	3	1

indeed the case for the lowest polymer molecular weight. The higher molecular weight probably makes small loops between its contact points. In the case of BSA, we found that the adsorption process is much less important than for ludox, N typically being 0.1. Here again, the area available per monomer is greater than 20 Å^2 and the chain probably adsorbs in a flat configuration. On the other hand, the adsorption in the case of the viruses was so important that we had to use a different method to evaluate c_a. We have already seen in *Table 2* that the ξ values obtained from the experiments on viruses are much too large. With a 1×10^{-2} g/cm^3 concentration of $M = 300\,000$ polymer: $\xi = 130$ Å for an EMV virus concentration of 3×10^{-3} g/cm^3; $\xi = 240$ Å for a TBSV virus concentration of 3×10^{-3} g/cm^3, to be compared with a true value of 31 Å.

These ξ values correspond to $c_e \simeq 10^{-3}$ g/cm^3 ($c_a \simeq 9 \times 10^{-3}$ g/cm^3) and $c_e \simeq 0.4 \times 10^{-3}$ g/cm^3 ($c_a = 9.6 \times 10^{-3}$ g/cm^3), respectively. Almost all the polymer has been absorbed on the virus surface. N is now of the order of 100.

Up to now we have not discussed the possibility of a single polymer chain absorbing simultaneously on several solid particles and forming bridges. It is generally assumed that this process is responsible for flocculation[23]. In our case, it would change the size of the sedimenting particles and thus the observed sedimentation rate. Actually a particle size increase would lead to an overall decrease in mobility. This could explain why the limiting value of the sedimentation coefficient for high polymer concentration is not related to the macroscopic solution viscosity (see above). However, it is striking to note that: (i) no flocculation has been observed and (ii) the sedimentation pattern contains only one narrow peak for the solid particles. This seems to exclude the existence of aggregated solid particles since they would be expected to have a wide size distribution. Moreover, an anomalous dependence of the sedimentation coefficient on the particle concentration has not been observed. At this stage it seems very difficult to draw a definite conclusion on this particular point, and more specific experiments are under way.

CONCLUSION

The experimental data reported here continue the earlier results obtained by Laurent *et al.*[6–8] and Ogston *et al.*[18]. However, the use of polymer materials with sharper mass distribution and the correction of the sedimentation data for polymer adsorption make the present experiments quantitatively more reliable.

It seems clear that the retardation factor s/s_0 follows a scaling law: $s/s_0 = \psi(R/\xi)$ with $\psi \sim 1$ for $R/\xi \ll 1$. ψ was found to be of the form $\exp(-Ac^y)$ as already observed by previous workers. However, the value of y is not 0.50 as assumed so far but markedly higher, $\simeq 0.62$ for PEO solutions. This last value is close to the exponent value of the coherence length *versus* concentration. $\xi \propto c^{-\nu}$ with $\nu = 0.75$ (ideal case)[2] or $\nu \simeq 0.67$ (from dynamic experiments on polystyrene solutions)[19]. The factor A is proportional to the particle radius, R, but independent of polymer molecular weight, contrary to what had been stated before.

Furthermore, an analysis of the dependence of sedimentation data on particle concentration has allowed us to gain information about the structure of the polymer layer adsorbed onto the particle surfaces. It has been possible to estimate the amount adsorbed, the number of adsorbed chains per particle, and an upper value for the adsorbed thickness.

On the other hand, it is clear that the R dependence of the sedimentation coefficient should be investigated more thoroughly. Also the experimental observation that at high polymer concentration the sedimentation coefficients do not converge towards a constant value proportional to the macroscopic viscosity, is still unclear. Further experiments are currently under way to elucidate these points.

At any rate, apart from theoretical interests, the necessity for a better understanding of such widely used techniques as gel electrophoresis and molecular sieve chromotography is a decisive impetus to pursue more experiments along these lines.

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