Conformation of gelatin chains in aqueous solutions: 2. A quasi-elastic light scattering study

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(*Received 1 August 1990; revised 8 October 1990; accepted 10 October 1990*)

We have characterized dilute and semi-dilute aqueous gelatin solutions by quasi-elastic light scattering. The concentration dependence of the scattering spectra has been explored. In semi-dilute solutions, two diffusive modes were determined: the fast mode, with a diffusion coefficient D_f, is attributed to the cooperative movements of the entangled transient network of chains and it increases with the concentration as $D_f \sim c^{0.6}$; the slow mode, whose diffusion coefficient D_s is inversely proportional to the Newtonian viscosity of the solution, is interpreted as the self-diffusion of clusters of chains that have a constant hydrodynamic radius $R_c \approx 750$ Å. The effects on the slow modes of the salt content of the solutions, the molecular weight of the chains and temperature are examined. Besides, it is shown that the addition of a surfactant (sodium dodecylsulphate) hinders the formation of the clusters, and it is concluded that the latter are probably stabilized by hydrophobic interactions between apolar lateral groups of the protein.

(Keywords: conformation; gelatin; solution; quasi-elastic light scattering; cooperative diffusion; slow mode)

INTRODUCTION

In this paper we examine the quasi-elastic light scattering (QELS) of gelatin solutions in the dilute and semi-dilute ranges. This investigation parallels the static light scattering (LS) and small-angle neutron scattering (SANS) investigation reported in the preceding paper[1], both types of experiments being necessary in order to elucidate the structure of gelatin solutions. QELS is an efficient tool to study polymeric and colloidal solutions. The scaling laws have provided a clear description of the time-dependent properties of polymeric solutions[2], in addition to their spatial arrangements. Although the dynamic regimes of flexible coils in good solvents are now well understood[3,4], it appears from the literature that a great number of polymeric solutions exhibit non-trivial correlation functions whose origin is still debated[5–9]. As the static scattering experiments in gelatin solutions revealed such complex effects, resort to QELS seems particularly suitable to test the various possible interpretations of these effects. A previous investigation by Amis *et al.*[10] has shown the difficulty of this task.

This paper first recalls the characteristics of the gelatin sample and of the experimental method, then briefly reviews the basic ideas in analysing the QELS spectra. The results are reported and discussed with emphasis on interpretation of the spectra of semi-dilute solutions, where two diffusive modes can be observed. The origin of the 'slow mode' of the semi-dilute solutions is thoroughly investigated.

EXPERIMENTAL

Sample characterization and preparation

The gelatin sample comes from lime processed demineralized ossein (Rousselot gelatin), kindly provided by Sanofi-Bio-Industries. The sample characterization and preparation has already been published[11]. The polydispersity index $M_w/M_n = 2.3$, with a weight-average molecular weight $M_w = 1.9 \times 10^5$ g mol^{-1}. This sample is a photographic grade type. The solvent is an aqueous solution of 0.1 M NaCl and the pH, initially equal to 5, was adjusted to pH 7: the salt ions screen out the electrostatic interactions between the charged groups of the protein chains and the neutral pH allows one to avoid the isoelectric point. A small amount of sodium azide (NaN_3) was added to prevent bacterial contamination. The gelatin granules were first allowed to swell in the solvent for 12 h at 4°C. Then, the mixture was heated to 50°C and gently stirred until dissolution was complete (1 h). Prior to the quasi-elastic light scattering measurements, the warm gelatin solutions were filtered through 0.45 μm Millipore filters to eliminate dust. No modification of the solution concentration due to filtration could be detected. Concentrations, expressed in g/g, were varied from 0.2 to 20%.

Dynamic light scattering

QELS was measured using a 64-channel real-time autocorrelator (7032 Multi-4 Malvern) interfaced to an Olivetti-M24 computer. The incident light was provided by a Spectra Physics He–Ne laser ($\lambda = 6328$ Å) with a light power of 22 mW. The scattered light was detected

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0032-3861/91/173211-07

with a photomultiplier tube (ITT FW 130) operating in the photon-counting mode. The goniometer sample holder (200SM from AMTEC) allows us to vary the scattering angle between 30° and 135°. The temperature of the scattering cell was regulated at 50 ± 0.1°C by an external bath. Experiments were performed in the homodyne mode[12].

We recall that the scattering vector q is given by:

$$q = (4\pi n/\lambda)\sin(\theta/2) \qquad (1)$$

where θ is the scattering angle, λ is the wavelength of the incident light *in vacuo* and n is the index of refraction of the solution.

BACKGROUND IN QELS OF POLYMERIC SOLUTIONS

We briefly recall the basic features of the QELS spectra of dilute and semi-dilute solutions.

The dilute range: $c/c^* \ll 1$

At very low concentrations c (dilute solution), i.e. c much less than the overlap concentration c^*, a macromolecular solution behaves as a collection of independent coils characterized by the z-average self-diffusion coefficient $\langle D_0 \rangle_z$, which is given by the Stokes–Einstein relationship:

$$\langle D_0 \rangle_z = \frac{k_B T}{6\pi\eta_0} \langle 1/R_h \rangle_z \qquad (2)$$

where k_B is the Boltzmann constant, T the absolute temperature, η_0 the viscosity of the solvent and R_h the hydrodynamic radius of the coil. The normalized autocorrelation functions, $g^{(2)}(\tau)$, where τ is the correlation time, can be interpreted as single-mode functions in dilute solutions. However, for polydisperse samples, these functions generally show a deviation from monoexponentiality, which can be analysed by the method of cumulants[12–14]. In this case $\ln|g^{(2)}(\tau) - 1|$ *versus* τ can be fitted to a third-order polynomial such as:

$$\ln|g^{(2)}(\tau) - 1| = \ln \alpha + 2\left(-\langle \Gamma \rangle \tau + \frac{1}{2!}\frac{\mu_2}{\langle \Gamma \rangle^2}(\langle \Gamma \rangle \tau)^2 - \frac{1}{3!}\frac{\mu_3}{\langle \Gamma \rangle^3}(\langle \Gamma \rangle \tau)^3 + \cdots \right) \qquad (3)$$

where $\langle \Gamma \rangle$ is the average decay rate of the correlation function, the coefficients μ_n are the different moments of the distribution of the decay rates, and α is the spatial coherence factor $(0 < \alpha < 1)$ taken as an adjustable parameter in the data-fitting procedure. The background associated with the d.c. component which normalizes the autocorrelation function is measured from the time-delayed channels of the correlator. The average decay rate $\langle \Gamma \rangle$ is proportional to the square of the scattering vector q^2, and the z-average self-diffusion coefficient $\langle D_0 \rangle_z$ of the coils is derived from the following relation[12]:

$$\langle \Gamma \rangle = \langle D_0 \rangle_z q^2 \qquad (4)$$

The semi-dilute range: $c/c^* > 1$

Above the overlap concentration, c^*, semi-dilute solutions exhibit collective motions, which are described by the cooperative diffusion coefficient D_{coop} related to the hydrodynamic correlation length ξ_h of the transient network of chains:

$$D_{\text{coop}} = \frac{k_B T}{6\pi\eta_0\xi_h} \qquad (5)$$

According to de Gennes[2], for a solution of flexible coils in a good solvent, ξ_h varies with the polymer concentration with the power law:

$$\xi_h \sim (c/c^*)^{-3/4} \qquad (6)$$

This law is independent of the molecular weight of the polymer.

RESULTS AND DISCUSSION

We have investigated the concentration dependence of the correlation functions of aqueous gelatin solutions. From the determination of the average molecular weight one can evaluate the overlap concentration $c^* \approx 0.5\%$. Below this limit, in the dilute range, the self-diffusion coefficient of the independent coils is derived from the spectra. Using the third-order cumulant method (equation (3)), we found $\langle D_0 \rangle_z = 2 \times 10^{-7}\ \text{cm}^2\ \text{s}^{-1}$, which gives an equivalent hydrodynamic radius of the chains $R_h = 220$ Å. For linear chains, it is known that the hydrodynamic radius is smaller than the radius of gyration. For gelatin coils, we found[1] $R_g = 330 \pm 30$ Å and the ratio $R_g/R_h = 1.5$. This ratio is expected to depend on the chain configuration (linear or branched chains), on the molecular weight, on the solvent quality and on the polydispersity index. For polydisperse linear chains with a polydispersity index of about 2 and with a Schulz–Zimm distribution, Burchard[15] predicts a ratio of 1.72. By taking into account the excluded-volume effects from the theory of Weill and des Cloiseaux[16], one can derive a value of 1.86 for a linear chain in a good solvent. In general, the experimental values[17,18] are found to be lower than predicted from the different theories. Our measurements are in good agreement with the existing literature in this field.

In the semi-dilute range, the decay of the correlation function cannot be analysed using the cumulant method with one average decay rate. In *Figure 1* we have plotted $|g^{(2)}(\tau) - 1|$ *versus* $\log \tau$ for two concentrations: $c < c^*$ (*Figure 1a*) and $c > c^*$ (*Figure 1b*). One can see in *Figure 1b* that the correlation function in the semi-dilute solution is composed of at least two dynamic modes, which differ by more than an order of magnitude. Thus, for semi-dilute solutions we have performed a two-mode analysis of the data. With the homodyne detection, we attempted to fit the correlation function $g^{(2)}(\tau)$ with a sum of two exponentials squared corresponding to the two relaxation modes, such as:

$$g^{(2)}(\tau) = 1 + \alpha[A_f(q)\exp(-\Gamma_f\tau) + A_s(q)\exp(-\Gamma_s\tau)]^2 \qquad (7)$$

We call Γ_f the characteristic decay rate of the fast mode and Γ_s the decay rate of the slow mode, $\Gamma_f > \Gamma_s$, with $A_f(q)$ and $A_s(q)$ being respectively the normalized amplitudes of these modes ($A_f + A_s = 1$). The ratio Γ_f/Γ_s being approximately 100/1, it was necessary to run two independent measurements for each scattering vector. When Γ_s can be neglected compared with Γ_f, equation

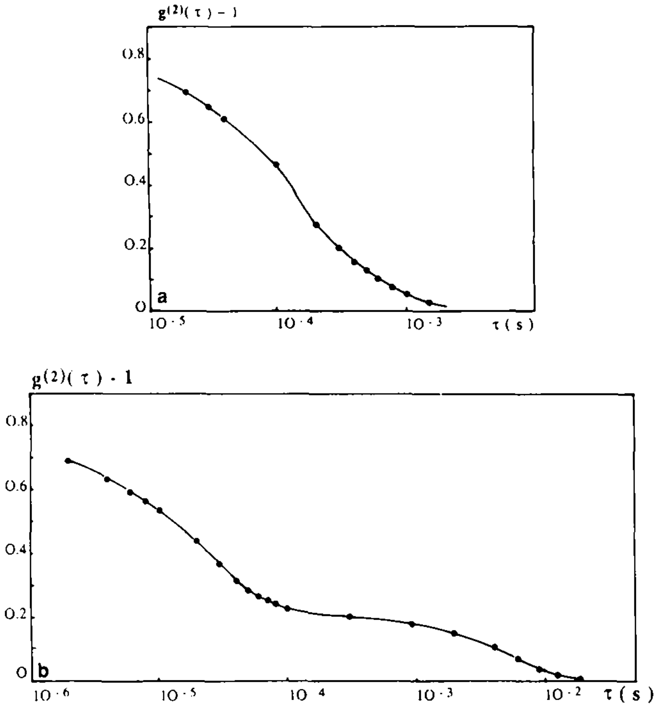

Figure 1 Two normalized correlation functions of gelatin solutions at $T = 50°C$ in dilute and semi-dilute ranges: the correlation functions are plotted *versus* the logarithm of the correlation time: (a) $c < c^*$, one relaxation mode appears in this case ($c = 0.1\%$, $\theta = 90°$); (b) $c > c^*$, the reconstructed correlation function clearly shows two relaxation modes separated by at least two orders of magnitude ($c = 10\%$, $\theta = 90°$)

(7) can be approximated by:

$$g^{(2)}(\tau) = \frac{G^{(2)}(\tau)}{G^{(2)}(\infty)}$$

$$= 1 + \alpha\{A_f(q)^2[F(\tau)]^2 + 2A_f(q)A_s(q)[F(\tau)] + A_s(q)^2 \exp(-2\Gamma_s\tau)\} \qquad (8)$$

where

$$F(\tau) = \exp(-\Gamma_f\tau) \qquad (9)$$

and $G^{(2)}(\tau)$ is the measured correlation function.

In order to analyse the two ranges of correlation times, we have defined an intermediate time τ_{int} such that $\tau_{int}\Gamma_f \approx 4$.

(i) For $\tau > \tau_{int}$ (the long-timescale experiment), $g^{(2)}(\tau)$ can be fitted as a single exponential:

$$g^{(2)}(\tau) = \frac{G^{(2)}(\tau)}{G^{(2)}(\infty)} \approx 1 + \alpha A_s(q)^2 \exp(-2\Gamma_s\tau) \qquad (10)$$

Experimentally, $G^{(2)}(\tau)$ was obtained with sampling times $\Delta\tau \approx 200$–$500\ \mu s$ and the first points were rejected. The baseline $G^{(2)}(\infty)$ was measured from the delayed channels and Γ_s was derived using the cumulants.

(ii) For $\tau < \tau_{int}$, the short-timescale experiment corresponding to $\Delta\tau \approx 2$–$10\ \mu s$, equation (8) can be written as a second-order polynomial in $F(\tau)$. The values of $G^{(2)}(\infty)$ and Γ_s are known from the long-timescale experiment, and $A_f(q)$ and $A_s(q)$ are derived making the assumption that $\tau_{int}\Gamma_f \ll 1$. From the short-time experiment, one is then able to calculate $F(\tau)$ for each value of τ (64 channels). We found that $\ln F(\tau)$ was linear *versus* τ and its slope gave Γ_f. This is shown in *Figure 2*. The linear regression coefficient r was typically $r \approx 0.998$. In the semi-dilute solutions, both the fast and the slow modes derived by this procedure appear as diffusive processes, as shown in *Figures 3* and *4*, where the Γ values are plotted *versus* q^2 for various concentrations in the semi-dilute range. The corresponding diffusion coefficients D_f and D_s are represented in *Figure 5 versus* concentration. The fast diffusion coefficient D_f increases with the polymer concentration, while the slow diffusion coefficient D_s decreases with increasing concentration. The ratio of the amplitudes A_s/A_f decreases with scattering angle and with concentration, as shown in *Figure 6*. The ratio varies between 0.5 and 1: the scattering due to the slowly relaxing mode is not dominating in any case (see below).

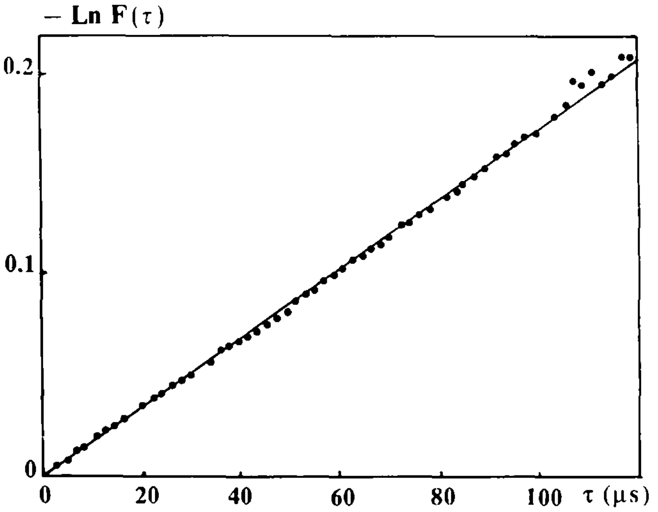

Figure 2 Two-mode data analysis: according to equation (8), $-\ln F(\tau)$ is plotted *versus* the correlation time τ. The slope of the straight line gives the relaxation rate $\Gamma_f = 1.6 \times 10^3\ s^{-1}$ of the fast mode for $c = 4\%$, $\theta = 90°$. The linear regression coefficient for this plot is $r = 0.998$

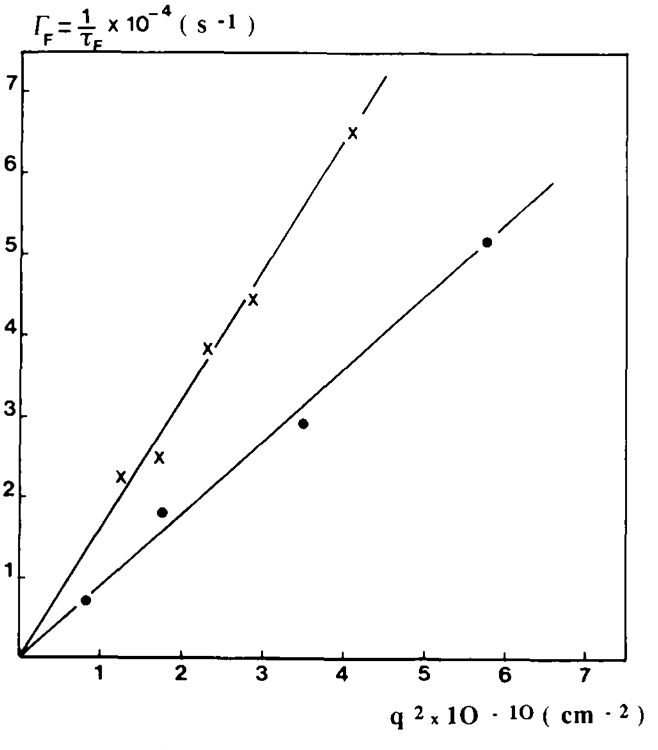

Figure 3 The q^2 dependence of the relaxation rate Γ_f for concentrations $c = 9\%$ (●) and $c = 16.6\%$ (×)

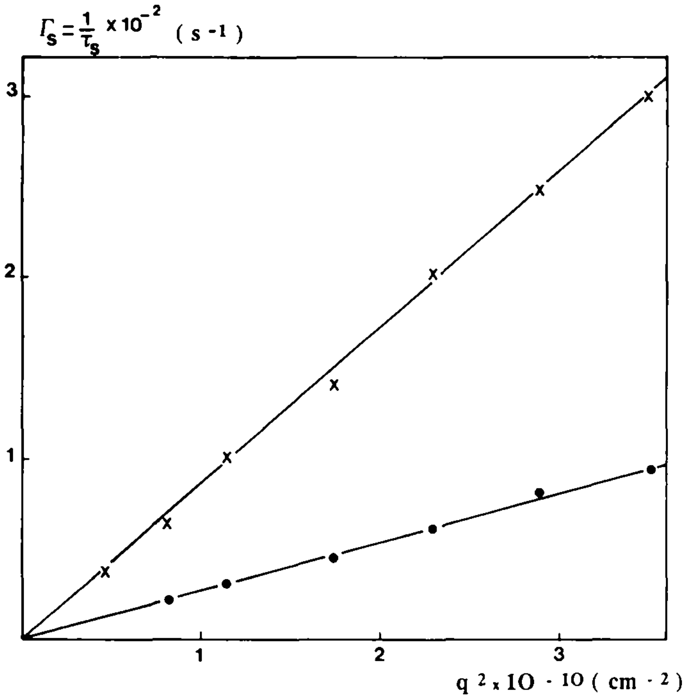

Figure 4 The q^2 dependence of the relaxation rate Γ_s for concentrations c = 4.8% (×) and c = 9% (●)

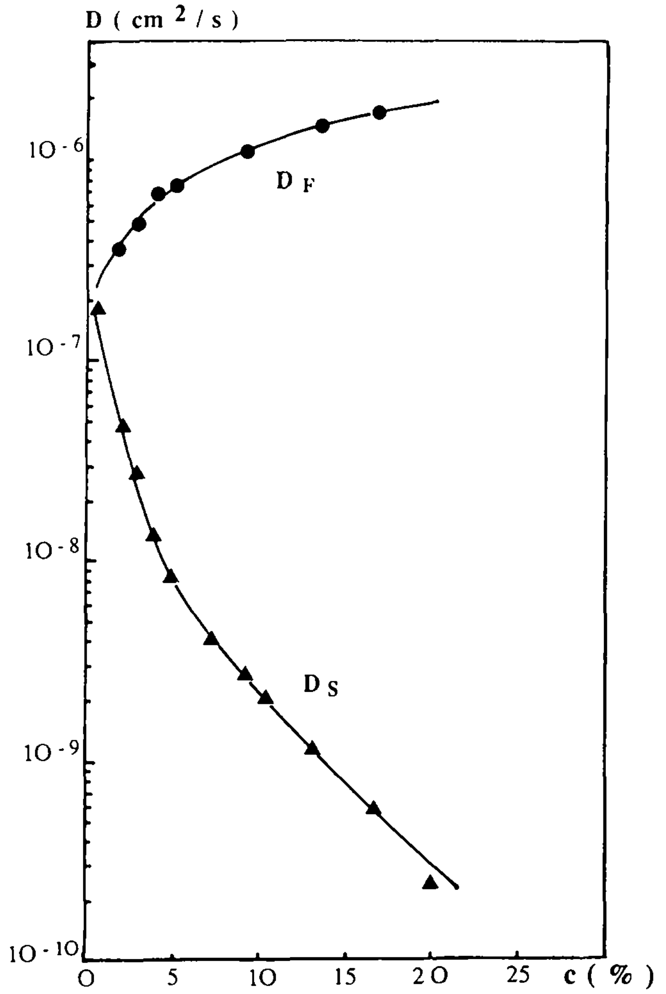

Figure 5 Semilogarithmic plots of the concentration dependence of the diffusive fast (D_f) and slow (D_s) modes. The full curves are guides for the eye

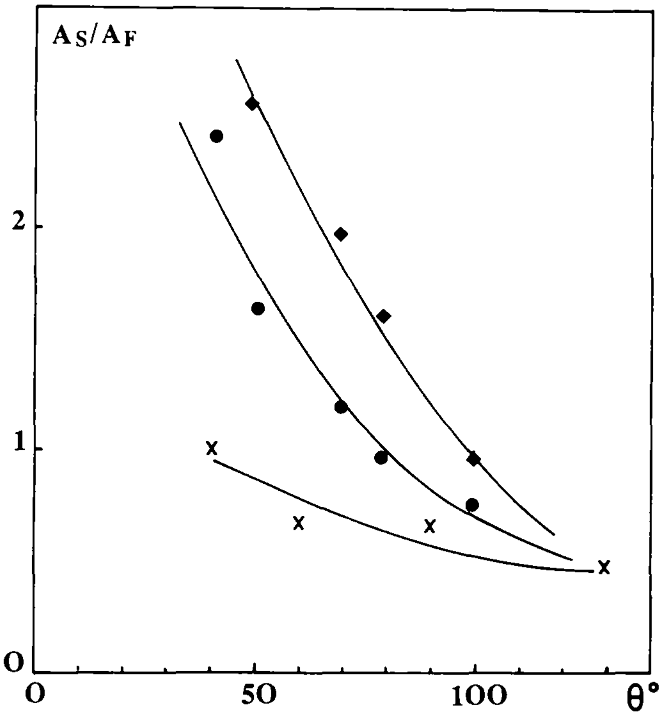

Figure 6 Ratio of the amplitudes A_s/A_f *versus* scattering angle θ for different concentrations: decreasing the scattering angle enhances the amplitude of the slow mode and increasing concentration also increases the relative amplitude of the slow mode. Three concentrations are shown: c = 9% (×), c = 13% (●) and c = 16.6% (◆). The full curves are guides for the eye

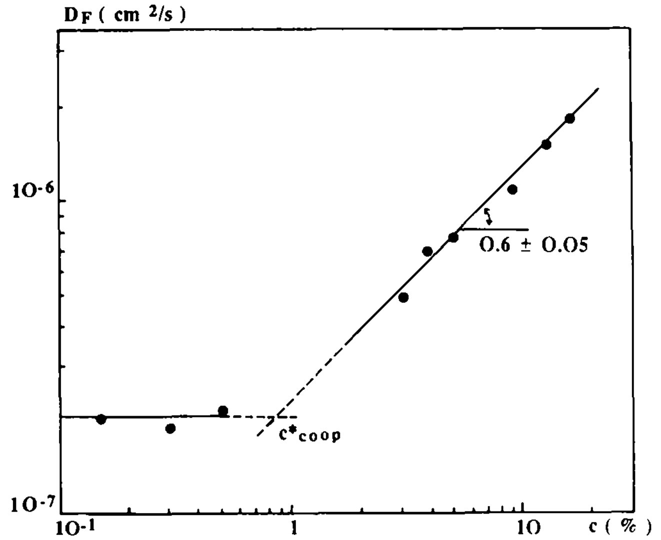

Figure 7 Fast diffusion coefficient D_f *versus* concentration in a double logarithmic plot. The slope of the straight line is equal to 0.6 ± 0.05. The fast diffusion coefficient D_f follows the theoretical predictions of the cooperative diffusion coefficient D_{coop}

The fast mode

The concentration dependence of the fast diffusion coefficient D_f is consistent with the predictions of the scaling laws for the cooperative diffusion coefficients in a good solvent. In *Figure 7*, D_f is plotted in a double logarithmic scale *versus* gelatin concentration. As stated before, two different regions appear: for $c < c^*$, the diffusion coefficient is independent of the concentration; and at higher polymer concentrations, $c > c^*$, a power-law behaviour is observed:

$$D_f = D_{coop} = \langle D_0 \rangle_z (c/c^*_{coop})^{0.6 \pm 0.05} \qquad (11)$$

The value of c^*_{coop} determined by extrapolating the data between the two regimes is about 0.8%. The data analysis does not allow us to determine D_f accurately in the range 1 to 3%. The concentration range that is reported here, $3\% \leqslant c \leqslant 11\%$, corresponds to $3.7 \leqslant (c/c^*_{\text{coop}}) \leqslant 13.7$. According to the theory of semi-dilute solutions, the cooperative diffusion coefficient is related to the hydrodynamic correlation length ξ_h of the transient network given by equation (6). The hydrodynamic screening length ξ_h varies in the range $25 < \xi_h < 100$ Å for concentrations decreasing from 15 to 5%. The power-law exponent (0.6) for D_{coop} is lower than predicted by the scaling theory (0.75). However, it is in agreement with the measurements of the static screening length ξ, derived by Pezron *et al.*[1], from SANS experiments. The scaling exponent calculated from either D_{coop} or ξ suggests a marginal solvent behaviour according to the model of Schaefer *et al.*[19].

The slow mode

The origin of the slowly relaxing mode is not well understood. Nevertheless, because of the numerous experimental studies[7–10] that have been carried out during the last decade on semi-dilute solutions, we are at least in a position now to discard some hypotheses regarding its origin. The slow mode is sample-dependent and not an intrinsic property of semi-dilute polymeric solutions, as pointed out by Balloge and Tirrell[7]. It should not be ascribed to polydispersity. Chang and Yu[20] have associated the slow mode in gelation solutions to the self-diffusion of individual chains, but a comparison of D_s with independently determined values of the self-diffusion coefficients (by pulsed-field-gradient n.m.r.[21] or forced Rayleigh scattering) has shown that the latter represents a considerably faster process. Other authors have interpreted the slow mode as the hindered movement through the solution of groups of entangled coils, also called 'clusters'[5]. This interpretation is likely to hold for gelatin solutions. Indeed, the following experiments have provided evidence for it: We first prepared a semi-dilute solution, then rediluted it and gently stirred it for several minutes; in the rediluted solution, the concentration was below 0.5%. For such a concentration a single-mode diffusion was expected to occur. However, for this 'dilute solution' the autocorrelation function did not exhibit a single relaxation rate, but two modes, which were both diffusive. This is shown in *Figure 8* where the diffusion coefficients of the two modes are displayed as a function of q^2 for a 0.3% gelatin solution prepared by diluting a 10% solution. Measurements were run for scattering angles between 40° and 90°. The faster of the two modes corresponds to the self-diffusion of single gelatin coils. Using the Stokes Einstein relation with $D_f = 2.1 \times 10^{-7}$ cm^2 s^{-1}, $\eta_0 = 0.54$ cP and $T = 50$°C, we found $R_h = 210$ Å, which corresponds to the previously determined hydrodynamic radius of the free gelatin coils in the dilute range. Regarding the slower mode in *Figure 8*, the Stokes Einstein relation allows us to determine a hydrodynamic radius R_c for the 'clusters'. If one considers for these large particles the macroscopic viscosity of the dilute solution, $\eta_{\text{macro}} \approx 1$ cP, and $D_s = 3.5 \times 10^{-8}$ cm^2 s^{-1}, then one finds an effective radius $R_c = 850 \pm 80$ Å. In this type of experiment, we did not observe any difference in the diffusion coefficients of the clusters when a 0.3% solution was obtained from a 15% solution. Thus, the initial concentration of the semi-dilute gelatin solution does not seem to affect the size of the clusters. This is corroborated by direct investigation of the semi-dilute solutions: indeed in the range of concentrations 5 to 20% we have plotted the slow diffusion coeffcients D_s *versus* the inverse of the macroscopic viscosity of the solution (measured with a Rheomat 30 Contraves instrument). The Newtonian viscosities of the solutions vary approximately from 3 to 35 cP. A linear relationship is observed in *Figure 9*. Thus, we may ascribe

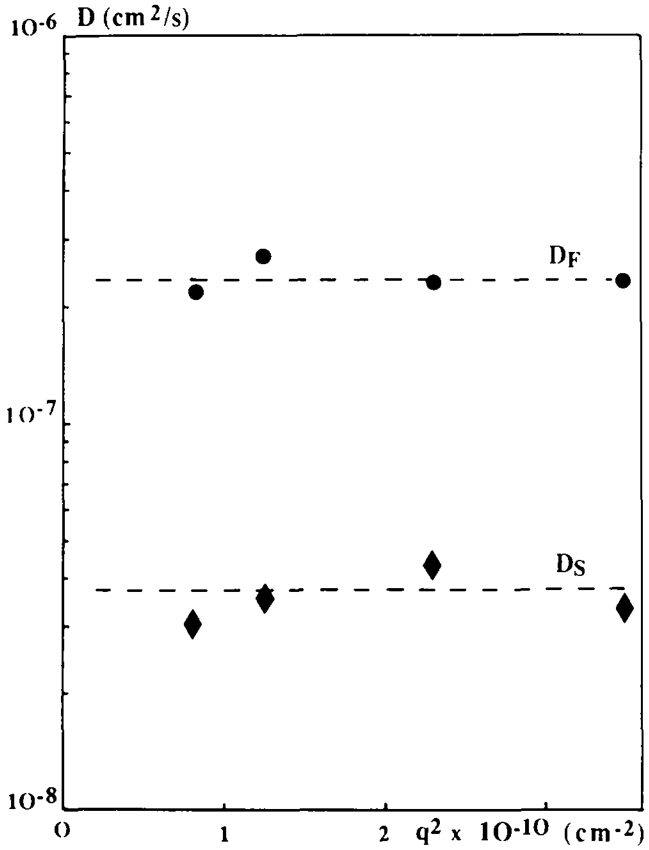

Figure 8 A redilution experiment: a $c = 0.3\%$ solution was prepared by diluting a $c = 10\%$ solution at $T = 50$ C. Two diffusive modes are observed: the faster, D_f, is the self-diffusion of the gelatin coils and the slower, D_s, corresponds to the diffusion of clusters of chains. The same scattering spectrum persisted after 24 h. However, when this solution was subjected to a mild continuous stirring for 2 h, the clusters could be dispersed

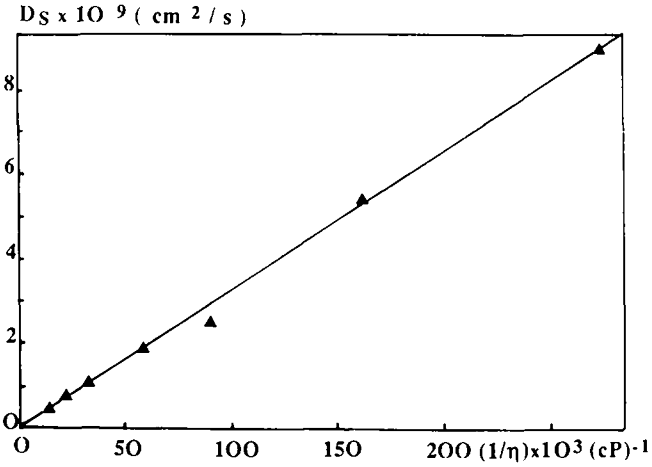

Figure 9 The plot of the slow diffusion coefficient *versus* the inverse of the macroscopic viscosity of the solution allows one to calculate the hydrodynamic radius R_c of the clusters: $R_c = 725 \pm 40$ Å

the slow mode in the semi-dilute solutions to clusters of chains of a constant size, diffusing through a medium of viscosity η_{macro}. Using again the Stokes–Einstein relationship, we can deduce R_c in the semi-dilute solutions: $R_c = 725 \pm 40$ Å, which is consistent with the value derived from the redilution experiments.

The important enhancement of LS and SANS, as compared to the scattering of a 'normal' semi-dilute solution in a good solvent, reported in the previous paper[1], is also in agreement with the assumption that these solutions contain a few large clusters. Moreover, the observed angular dependence of the slow mode, A_s, assuming that the amplitude of the fast mode is independent of the scattering angle, indicates the presence of scatterers whose size is of the order of q^{-1} (500–1000 Å). Thus, the orders of magnitude derived from both techniques agree. A more quantitative comparison between the average radii of the clusters (R_h and R_g) should involve a precise description of the structure of the clusters. Some subtle effects due to the density contrast between the clusters and the solution may be relevant as well.

In conclusion, slow modes measure the self-diffusion of clusters through either a semi-dilute or a rediluted gelatin solution.

Nature of the clusters

One can presume that the clusters are formed by strongly interacting gelatin chains. They were stable upon dilution and were still detected even after 24 h in the rediluted solutions. The clusters, however, could be dispersed under a mild stirring for 2 h at 50°C and the solution again recovered the scattering of a dilute, well dissolved sample.

A temperature increase in the range $40 < T < 80$°C does not affect the presence or the size of the clusters. This was checked by measuring both D_s and the viscosity of the solution at different temperatures.

We have also investigated the influence of the nature or amount of salt in the aqueous solvent: 0.1 M LiBr and KSCN solutions were prepared; these salts are known as hydrogen-bond-disrupting agents. In these solutions no gelation occurs even at 10°C. However, these salts do not affect the decay rate of the slow mode at $c = 10\%$. When the concentration of NaCl was raised to 1.5 M, no substantial changes of the slow mode could be detected either.

We also explored the influence of the molecular weight of the gelatin sample: for lower molecular weights we noticed a slight decrease of the hydrodynamic radius of the clusters: for a sample with $M_w = 4.2 \times 10^4$ g mol^{-1} we found $R_c = 700$ Å, and for $M_w = 3.1 \times 10^4$ g mol^{-1}, $R_c = 600$ Å.

The only attempt which succeeded in substantially modifying the slow modes was the addition of a surfactant, sodium dodecylsulphate (SDS). In these experiments, we made a 0.1 M NaCl solution with 10% of gelatin at pH = 7 with 18 g l^{-1} of SDS. Then, the solution was dispersed with a 0.1 M NaCl aqueous solvent, so that the final concentration was 0.1% in gelatin and 0.018% in SDS (or 6×10^{-4} M in SDS). The SDS concentration is well below the critical micellar concentration (8×10^{-3} M). In *Figure 10* one can see the normalized correlation functions of a rediluted solution, in the presence and absence of SDS, for long correlation times. The modifications of the slow mode are obvious: no slow mode was detected in the presence of SDS. The diffusion coefficient derived in the latter case is equal to 1.7×10^{-7} cm^2 s^{-1}. This value is slightly below the diffusion coefficient of the gelatin single coils; this difference can be ascribed to an increase of size of the gelatin coils due to adsorption of SDS or to a change of the solution viscosity.

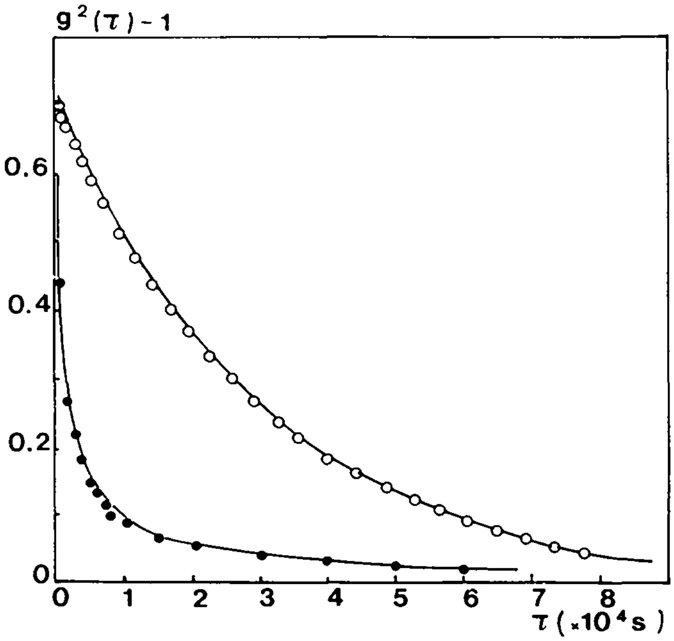

Figure 10 The normalized correlation function of a $c = 0.1\%$ solution prepared by rediluting a $c = 10\%$ solution: (○) without SDS; (●) with an initial concentration of SDS of 18 g l^{-1}. In the second case, no slow mode could be detected in the 'dilute solution'

CONCLUSIONS

This investigation of the dynamic modes of dilute and semi-dilute gelatin solutions corroborates the results obtained by LS and SANS and reported in the preceding paper. Both types of experiments establish essentially that in the semi-dilute solutions clusters of chains form spontaneously. The existence of the slowly relaxing mode in this concentration range had already been pointed out by Amis *et al.*[10], although no reliable interpretation has been proposed for it. In particular, the linear variation of the diffusion coefficient of the slow mode with the inverse of viscosity was also reported in their paper (the molecular weight of their sample being close to $M_n = 35000$ g mol^{-1}). From this investigation, we can conclude that the slow mode can be ascribed to the self-diffusion of a few clusters through the rest of the solution. The clusters are remarkably resistant to redilutions, to temperature increase and to salt addition. Their size depends slightly on the molecular weight of the chains; the clusters are dispersed by an anionic surfactant (SDS). The type of interactions that stabilize the clusters are of neither an electrostatic nor hydrogen bonding nature. The sensitivity to surfactants inclines towards hydrophobic interactions. Indeed, the apolar lateral groups of some amino acids of the collagen protein (like proline (12%), alanine (10%), leucine and isoleucine (3%)) provide specific sites for interchain association in the semi-dilute range. In the presence of a surfactant, these sites may in preference be surrounded by surfactant molecules, thus hindering the process of interchain clustering.

Gelation is obtained by quenching the semi-dilute solutions below 28°C. It can also be investigated by QELS: the preliminary results[22] show mostly that the slow mode is considerably slowed down through the sol–gel transition, while the fast mode is almost unperturbed. Similar observations have been reported by Munch *et al.*[23] during a radical copolymerization reaction. Using rheological experiments, we have shown that the dramatic increase of the correlation time of the slow mode parallels the increase of the elastic shear modulus of the gel; this phenomenon is due to the complex diffusion of the scatterers through the gel network.

ACKNOWLEDGEMENT

This investigation has been partly supported by Sanofi-Bio-Industries.

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