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Static and dynamic light scattering study of strong intermolecular interactions in aqueous solutions of PVP/C_{60} complexes

Maria L. Sushko[a,b,*], Heikki Tenhu[a], Stanislav I. Klenin[b]

[a]Laboratory of Polymer Chemistry, University of Helsinki, PB 55, FIN-00014 HY, Helsinki, Finland
[b]Institute of Macromolecular Compounds, Russian Academy of Science, Bolshoi Prospect 31, 199004 St Petersburg, Russian Federation

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Abstract

The investigations of the dilute aqueous solutions of polyvinylpyrrolidone/fullerene (PVP/C_{60}) complexes by static (SLS) and dynamic (DLS) light scattering showed that strong intermolecular interactions, effective on the distances of about 45–50 nm, take place in the solutions. Two concentration ranges are well distinguished in these solutions. Above a critical concentration (c_{cr}) the fluctuations in the solutions are hindered and only one, diffusive, mode is observed in DLS experiments. Upon dilution ($c < c_{cr}$) this unified structure divides into large fragments (domains) and the slow mode attributed to long-range concentration fluctuations, gradually appears. The angular and concentration dependencies of the diffusion coefficient of the slow mode indicate the existence of strong intermolecular interactions. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Dynamic light scattering; Intermolecular interactions; Fullerene–polymer complexes

1. Introduction

Properties of fullerene solutions in different solvents attract much attention. Aqueous solutions of fullerene are very important from the practical point of view because of their possible application in biology. To keep fullerene in an aqueous medium it may be derivatized or complexed with hydrophilic polymers. The last method seems to be more favorable because in this case, the initial structure of fullerene is almost intact and, consequently, the biological activity of such samples is higher than that of samples with covalent bonds [1,2]. NMR experiments revealed that complexes of polyvinylpyrrolidone, PVP, with fullerene are formed via donor–acceptor bonds between the carbonyl groups of the polymer and fullerene [1]. About 4–6 repeating units of PVP are found to interact with one fullerene molecule. Hydrophilic repulsion between PVP molecules competes with the tendency of hydrophobic fullerenes to aggregate in aqueous media and strong intermolecular interactions have been detected in static light scattering experiments in dilute aqueous solutions of PVP/C_{60} complexes [3–5]. This makes it possible to investigate the effect of long-range interactions in these solutions on the shape of the intensity-time correlation function by dynamic light scattering (DLS) and compare the results obtained with the theory of DLS for the systems with strong intermolecular interactions. Most of the experimental studies of this problem were recently performed in salt-free polyelectrolyte solutions [6–9]. However, the intermolecular interactions in polyelectrolyte systems are significant (two diffusive modes are observed) only in a very narrow region of concentrations below the overlap concentration and in the semidilute regime and thus, the effect of overlapping of the polymer chains should also be taken into account. In the case of the solutions of PVP/C_{60} complexes, intermolecular interactions are effective even in very dilute regime and this allows one to investigate the effects of interactions in their pure form. To our knowledge this is the first experimental study of the sort.

2. Experimental

2.1. Materials

PVP/C_{60} complexes were synthesized by method described by Yamakoshi [10] in the Institute of Experimental Medicine RAMS, St Petersburg, Russia. Fullerene C_{60} of 99% of purity (‘Fullerene technologies’, Russia) and

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* Corresponding author. Present address: Department of Chemistry, Imperial College, Exhibition Road, London SW7 2AY, UK. Tel.: +44-020-7589-5111x55816; fax: +44-020-7594-5801.
E-mail address: m.sushko@ic.ac.uk (M.L. Sushko).

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almost monodisperse PVP with molecular weights 3×10^3 (synthesized in the Institute of Macromolecular Compounds RAS), 10×10^3 (Serva), 20×10^3 (Merck), 35×10^3 (synthesized in the Institute of Macromolecular Compounds RAS), and 40×10^3 (Sigma) were used. All polymers were characterized by static light scattering in aqueous solutions, M_w/M_n was found to be lower than 1.1 for all the samples. Two series of complexes with fullerene content 0.3 and 0.8 wt% were prepared, where the molecular weight of PVP was varied. Fullerene content in the complexes was determined from the UV absorption spectra of the samples in aqueous solutions. The complexes were dissolved in deionized water; concentrations ranged from 0.3 to 3.0 mg/ml. The solutions were purified with millipore 0.22 μm pore-size filters.

2.2. Instrumentation

Static light scattering (SLS) and dynamic light scattering (DLS) were performed with a Brookhaven instrument BI-200SM goniometer and BI-9000AT digital correlator. An Ar-ion laser (LEXEL 85, 1 W) operating at 514.5 nm wavelength was used as the light source. In dynamic light scattering experiments the time autocorrelation function of the scattered light intensity $g_2(t) = \langle I(0)I(t)\rangle$ was measured at scattering angles 45–150°. Correlation function $g_2(t)$ was converted to the scattered electric field autocorrelation function $g_1(t)$ via the Siegert relation [11]

$$g_1(t) = \{[g_2(t) - B]/B\}^{1/2} \tag{1}$$

where B is the experimentally determined baseline.

The shortest sample time varied from 2 to 2.4 μs, and the last delay varied from 8 to 15 ms. The number of correlator channels was 205. Data analysis was made using Brookhaven Instruments software (6KDLSW, Beta version 1.30). Time correlation functions were analyzed with program CONTIN (version 1.60) by fitting correlation curves as

$$g_1(t) = \int_0^\infty A(\tau)e^{-t/\tau}\,d\tau \tag{2}$$

where $A(\tau)$ is a distribution function of decay times. Diffusion coefficients were calculated as $D_i = (1/\tau_i)q^{-2}$ where q is the scattering vector defined as $q = (4\pi n/\lambda)\sin(\theta/2)$, with n, the solution refractive index, λ, the laser wavelength, and θ, the scattering angle.

The reduced scattering intensities cK/I_θ, where K, the optical constant, c, the concentration of the solution, and I_θ, the intensity of scattered light at angle θ, were calculated according to standard procedure using toluene as a reference with known absolute scattering intensity. The range of angles used was 30–150°.

3. Results and discussion

The results of static light scattering investigations of the solutions of PVP/C_{60} complexes show that the profile of the concentration dependence of the reciprocal intensity for these solutions has an unusual character (Fig. 1). Two regions are well distinguished in the investigated concentration range. When $c > c_{cr} = 1.45$ mg/ml I_{90} is almost independent of concentration (extrapolation to $c \rightarrow 0$ leads to $M \rightarrow \infty$). At concentration range $c < c_{cr}$ the extrapolation to a zero concentration leads to a finite quantity of M_w, which is, however, by 2.5 orders of magnitude greater than that for the matrix-polymer. However, practically no angular dependence of scattered light intensity is observed in the solutions. In other words, the radius of gyration of the scattering object with the molecular weight of the order of 10^6 cannot be determined from the Zimm plot. This means that the obtained results cannot be explained using the classical fluctuation theory of light scattering. This theory is valid for solutions of noninteracting scatterers. Instead, our results could be understood using the theory of static light scattering for interacting particles. The general equation for the intensity of scattered light for point like scatterers in this case is

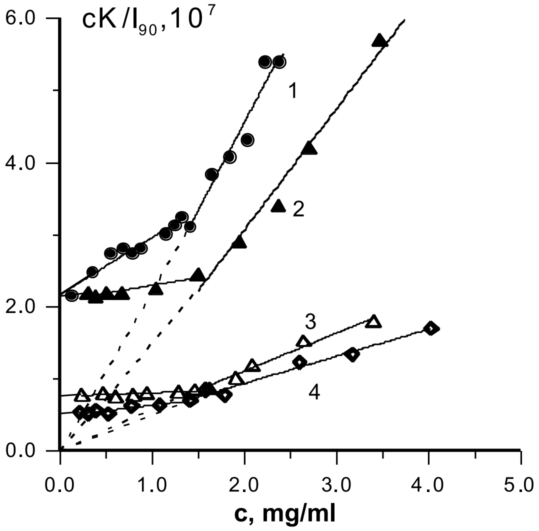

Fig. 1. Concentration dependence of $(cK/I)_{90}$ for aqueous PVP/C_{60} solutions with fullerene content 0.8% and molecular weight of matrix-polymer 10×10^3 (curve 1), 20×10^3 (curve 2), 35×10^3 (curve 3), 40×10^3 (curve 4).

$$\langle I_s\rangle = B^2\langle\alpha\rangle^2 V\rho_s S(\mathbf{q}, \rho_s) \tag{3}$$

where B is the constant not depending on the properties of the N scattering particles in the volume V of the solution, $\langle\alpha\rangle$ is the average polarizability, ρ_s is the average number density of the solute in the scattering volume V. The static structure factor $S(\mathbf{q}, \rho_s)$ is determined by the solute pair correlation function, $g(R)$, which depends only on the separation R of a pair of solutes:

$$S(\mathbf{q}, \rho_s) = \{1 - \rho_s \int_V d\mathbf{R}[1 - g(R)]\exp(i\mathbf{qR})\} \tag{4}$$

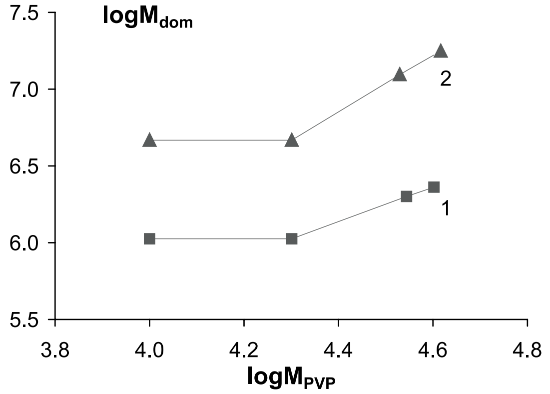

Fig. 2. Dependence of the molecular weight of domains in aqueous solutions of PVP/C_{60} complexes with fullerene content 0.3% (curve 1) and 0.8% (curve 2) on the molecular weight of PVP.

It can be seen from these equations that the intensity of scattered light for noninteracting scatterers (i.e. for the systems with $S(\mathbf{q},\rho_s)=1$) should be proportional to concentration, as is in general observed for most dilute polymer solutions. However, if interactions between the scatterers are strong enough, i.e. effective on the distances, comparable to intermacromolecular distances and the wavelength of light, the integral in the expression for the static structure factor is no longer negligible. In this case, the concentration dependence of the intensity of scattered light is a combination of an increasing (ρ_s) and a decreasing functions ($S(\mathbf{q},\rho_s)$) of concentration. Qualitatively, the contribution from the increase of fluctuations with concentration due to the increase of the number of scatterers in the unit volume will compete with the contribution of the decrease of fluctuations due to stronger intermolecular interactions at higher concentrations. This may lead to the observed independence of the intensity of scattered light on concentration, as shown in Fig. 1 when $c > c_{cr}$.

According to static light scattering results power β in a scaling relation $I \sim c^{\beta}$ for the solutions of PVP/C_{60} complexes is equal to zero in the concentration range $c > c_{cr}$ and $\beta = 1$ when $c < c_{cr}$. In other words, some noninteracting scattering objects, called as 'domains', are detected in the solution at $c < c_{cr}$, while they are not present at higher concentrations. Presumably at $c > c_{cr}$ the distances between the fullerenes are lower then the correlation length (ξ) and a certain, unified structure could be formed in the solution. Upon dilution, the distances between fullerenes gradually exceed ξ and the unified structure becomes unstable. We suppose that at $c < c_{cr}$ the unified structure, characteristic to the concentration range $c > c_{cr}$, is divided into fragments (domains) with the same structure and the same average distances between fullerenes (ξ), equal to about 45–50 nm at c_{cr}.

As it was pointed out above, the domains are independent scatterers and consequently, application of the classical theory is valid for calculation of the apparent molecular weight of the domains. However, the classical theory is not applicable to calculation of the radius of gyration of the domains due to strong correlation between the individual complexes *inside* a domain, affecting the angular dependence of the intensity of scattered light. The effect of intra-domain interference is the reason for the decreasing contributions to the angular dependence of the intensity, while the effect of strong interactions between the complexes inside the domain will give an increasing contribution (the static structure factor is a decreasing function of a scattering angle).

According to our experimental results, long-range fluctuations with the correlation length determined by the nature of intermolecular interactions and independent of the overall concentration of the complexes are present in the solutions of PVP/C_{60} complexes. We suppose that the unified structure is formed due to the balance of attraction forces between fullerenes and repulsion between the polymeric parts of the complexes, the latter being of entropic nature, i.e. excluded volume effect. It can be seen in Fig. 1 that the critical concentration, up to which a unified structure is observed, is the same for all samples with the same fullerene content in the complex, i.e. the critical distance between fullerenes where the balance of attractive–repulsive forces is achieved does not depend on the molecular weight of the matrix-polymer, nor on the whole concentration of the solution, nor on the fullerene content in the complex [4,5]. PVP influences the structure of the solution in a greater extent in the concentration range $c < c_{cr}$, when the unified structure is divided into large rather stable (second virial coefficient $A_2 \geq 0$) domains. It can be seen in Fig. 2 that the molecular weight of the domains (M_{dom}) is independent of the molecular weight of the matrix-polymer (M_{PVP}) when $M_{PVP} \leq 20 \times 10^3$ and a strong dependence $M_{dom} = (M_{PVP})^{\gamma}$ is observed when $M_{PVP} \geq 20 \times 10^3$. The calculations show that the contour length of PVP, L, with $M_{PVP} \geq 20 \times 10^3$ is higher than ξ, i.e. there is in principle a possibility of a fluctuation network formation due to entanglements between PVP molecules from neighboring complexes (Table 1). This additional type of interactions stabilizes the domains. The higher the contour length of PVP, the higher is the stabilization and the larger are the domains. This type of interactions does not play a role in the solutions of complexes on short PVP chains and thus, the dimensions of the domains are independent of M_{PVP} (Fig. 2).

Table 1
Characteristic properties of PVP/C_{60} complexes and their aqueous solutions (x is the fullerene content in the complexes)

M_{PVP} ($\times 10^{-3}$)	L (nm)	M_{dom} ($\times 10^{-6}$)	
		$x = 0.3\%$	$x = 0.8\%$
10	22.5	1.06	4.65
20	45.0	1.06	4.65
35	80.0	2.0	13.2
40	90.0	2.3	16.7

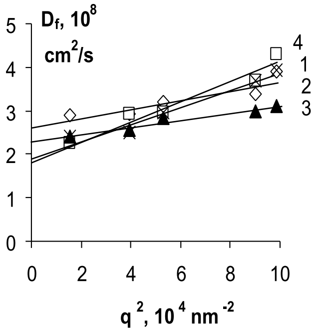

Fig. 3. The diffusion coefficient D_f plotted versus q^2 for PVP/C_{60} complexes with the molecular weight of matrix-polymer 3×10^3 (curve 1), 10×10^3 (curve 2), 20×10^3 (curve 3), 40×10^3 (curve 4) at concentration 2.7 mg/ml.

The power γ in the dependence $M_{\mathrm{dom}}=(M_{\mathrm{PVP}})^{\gamma}$ equals 1.56 when fullerene content in the complex is 0.8% while $\gamma=1.2$ when fullerene content in the complex is 0.3%. Presumably, for complexes with fullerene content 0.3% the number of polymer segments per fullerene molecule is higher and, consequently, higher is the probability of entanglement formation. Thus the dependence on the molecular weight of PVP is less distinct.

Dynamic light scattering measurements on the solutions of PVP/C_{60} complexes with fullerene content 0.3% showed that in concentration range $c > c_{\mathrm{cr}}$ the correlation function is single-exponential and the diffusion coefficient derived from the first cumulant is proportional to q^2 with a positive slope, i.e. it describes the diffusion of the complexes (Fig. 3). The magnitude of the self-diffusion coefficient of the complexes is, however, about 2 orders lower than that obtained from the translational diffusion measurements where a concentration gradient was applied to the solution and its initial structure was disturbed [4] (for example, the translational diffusion coefficient of PVP/C_{60} complexes with $M_{\mathrm{PVP}}=10\times10^3$ is equal to 1.0×10^{-6} cm^2/s). This result is consistent with the static light scattering data, according to which fluctuations in the solution are hindered in this concentration range. Thus the coefficient of self-diffusion obtained in the DLS experiments describes the hindered motion of the complexes in the organized solution.

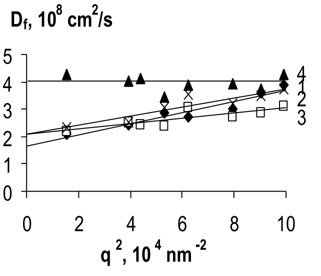

Fig. 4. The diffusion coefficient D_f plotted versus q^2 for PVP/C_{60} complexes with the molecular weight of matrix-polymer 3×10^3 (curve 1), 10×10^3 (curve 2), 20×10^3 (curve 3), 40×10^3 (curve 4) at concentration 1.0 mg/ml.

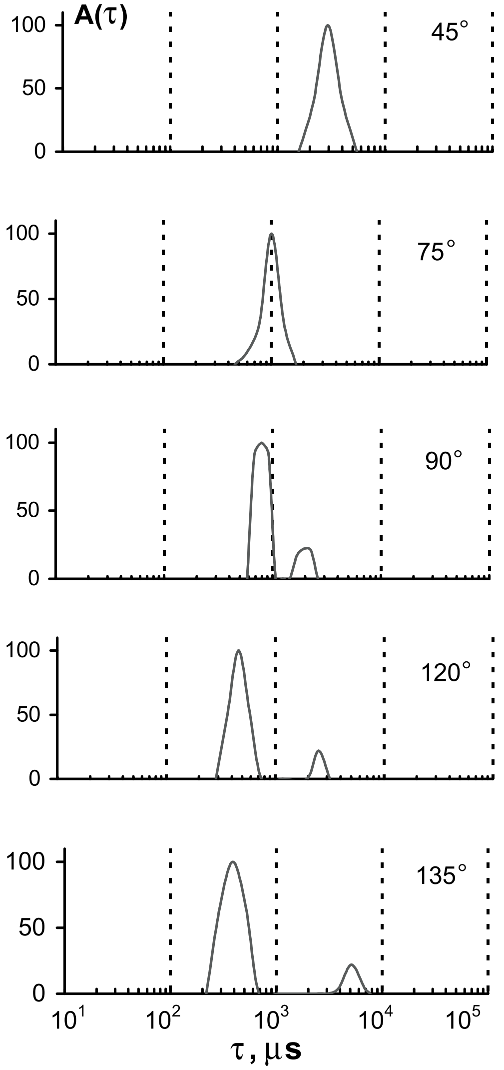

Fig. 5. Spectra of relaxation times obtained from dynamic light scattering experiments on aqueous solutions of PVP/C_{60} complex with $M_{\mathrm{PVP}}=20\times10^3$ and concentration 1.0 mg/ml. The scattering angles from top to bottom are 45, 75, 90, 120, and 135°.

At lower concentrations, $c < c_{\mathrm{cr}}$, the correlation function has a more complicated profile and a more complicated q-dependence. When the scattering angle is lower than 90° the main contribution is determined by the self-diffusion of the complexes, the correlation function has a single-exponential form and the diffusion coefficient of the complexes (D_f) in this concentration range is equal to that at $c > c_{\mathrm{cr}}$ and has the same q-dependence (Fig. 4). Thus D_f describes the motion of the complexes in the domains which presumably have the same structure as the solution at $c > c_{\mathrm{cr}}$. At $\theta = 90°$ the correlation function begins to deviate from a single-exponential form and along with the 'fast' mode a 'slow' mode appears (Fig. 5).

The deviation of the correlation function from a single-exponential form may be attributed to two, often competitive, effects: to the 'polydispersity' of the sample as well as to the presence of strong intermolecular interactions

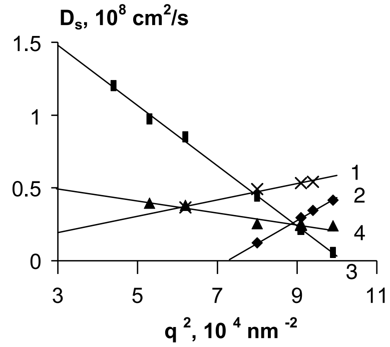

Fig. 6. The diffusion coefficient D_s plotted versus q^2 for PVP/C_{60} complexes with the molecular weight of matrix-polymer 3×10^3 (curve 1), 10×10^3 (curve 2), 20×10^3 (curve 3), 40×10^3 (curve 4) at concentration 1.0 mg/ml.

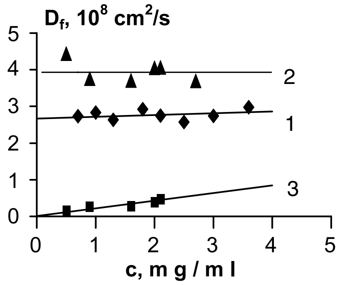

Fig. 7. Concentration dependence of D_f for the sample with $M_{PVP} = 10 \times 10^3$ at scattering angle 90° (curve 1), for the sample with $M_{PVP} = 40 \times 10^3$ at scattering angle 135° (curve 2), and D_s for the sample with $M_{PVP} = 40 \times 10^3$ at scattering angle 135° (curve 3).

effective on distances comparable with the wavelength of light and with intermolecular distances. In the case of the solutions of PVP/C_{60} complexes, both effects influence the profile of q-dependence of the diffusion coefficient of the slow mode (D_s). The polydispersity in this case is attributed to the presence of two types of scatterers in the solution: PVP/C_{60} complexes inside the domains and the domains, detected by static light scattering. Except the effect of polydispersity mentioned above the effect of strong intermolecular interactions should be taken into account. Thus, for our system the relaxation time distribution is expected to be three-modal. However, if the relaxation times corresponding to different modes are close to each other CONTIN will give only one peak in the spectra of relaxation times because the main principle of calculating the correlation function in CONTIN is to find the maximally smoothed function that still fits the experimental data. Presumably, the diffusion coefficient of the domains and that due to long-range interactions are close to each other and only two peaks are observed at high angles (Fig. 5). In these considerations, the first peak denotes the diffusion of the complexes with the diffusion coefficient $D_f \sim q^2$ and a positive slope. The second peak is attributed, as pointed out earlier, to two factors and the slope of the q-dependence of D_s is determined by a balance of these two factors.

In the case where the deviation of the correlation function from a single-exponentiality is only due to strong intermolecular interactions, the diffusion coefficient of the slow mode in isotropic systems is related to the diffusion coefficient at infinite dilution D_0, the static structure factor $S(q)$ and the concentration of the scattering particles ρ_s (expressed in particles per unit volume) by Ackerson equation [12]

$$D_s = [D_0/S(q)][1 + b(q)\rho_s] \tag{5}$$

here $b(q)$ is a q-dependent function determined by hydrodynamic interactions, which tend to zero in the high-q limit. For such a system Zernicke and Prins obtained the following expression for a static structure factor [13]

$$S(q,R) = \{1 - 4\pi\rho_s \int_0^a \mathrm{d}R\, R^2[1 - g(R)][\sin(qR)/qR]\} \tag{6}$$

Here $g(R)$, as above, is the solute pair correlation function, which for isotropic system depends only on the separation R of a pair of solute particles, i.e. $R = [(\mathbf{r}_i - \mathbf{r}_j)(\mathbf{r}_i - \mathbf{r}_j)]^{1/2}$, where $\mathbf{r}_i$ and $\mathbf{r}_j$ are the instantaneous positions of particle i and j, respectively. The integral in Eq. (6) is limited to a value of $R = a$, above which the pair correlation function does not significantly differ from unity (a can be called the range of interactions).

For the samples with the molecular weight of matrix-polymer equal to 20 and 40×10^3 $D_s(q^2)$ appeared to be a decreasing function of angle at high q in agreement with Eq. (5) (Fig. 6 curves 3,4). Consequently, for these solutions the effect of intermolecular interactions gives the main contribution to the angular dependence of D_s. It is noteworthy, that according to the scaling theory for systems with strong intermolecular interactions the slow mode is expected to appear when the value of $q\xi$, where ξ is the correlation length, is not much lower or higher than unity [13]. In our case the slow mode appears at $\theta = 80$–$90°$, i.e. at $\xi = 45$–50 nm. Thus we have shown by an independent method that the characteristic distance between the fullerenes is about 50 nm.

For the samples with lower molecular weight (3 and 10×10^3), for which there is a low probability of the entanglement formation, the pair correlation function $g(R)$ in Eq. (6) will be closer to unity and consequently q-dependence of D_s is mostly determined by the polydispersity contribution. In this case q-dependence of D_s has a positive slope characteristic to a diffusive process and D_s describes mostly the diffusion of domains (Fig. 6 curves 1,2). Data on the concentration dependence of D_f, shown in Fig. 7 (curves 1,2), are also consistent with the supposition of the presence of the long-range correlation between the complexes in the solution. Indeed, according to our model the motion of the complexes in the whole investigated concentration range proceeds in solutions with similar structures: in the solution with hindered fluctuations ($c > c_{cr}$) or inside the domains, which are the fragments of the former organization ($c < c_{cr}$). Thus no concentration dependence of D_f should be observed (see Fig. 7). However, the diffusion coefficient of the slow

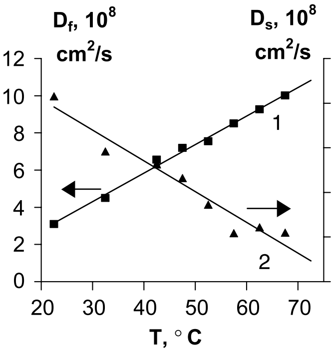

Fig. 8. Temperature dependence of D_f (1) and D_s (2) for the sample with $M_{PVP} = 10 \times 10^3$ at scattering angle 150°.

mode, D_s, for the sample with $M_{PVP} = 40 \times 10^3$, i.e. for the sample for which the deviation of the correlation function from the single-exponential form is mostly due to strong intermolecular interactions, shows a distinct concentration dependence (Fig. 7 curve 3). This result is consistent with the theory of DLS for the systems with strong intermolecular interactions. According to Eqs. (5) and (6), the diffusion coefficient stipulated by interactions is a monotonically increasing function of concentration (note that $[1/S(q)]$ is an increasing function of concentration).

Thus according to the dynamic light scattering results on aqueous solutions of PVP/C_{60} complexes in the case when the deviation of $g_1(t)$ from a single-exponential form is mostly attributed to strong intermolecular interactions, the concentration and q-dependencies of the diffusion coefficient D_s are in good agreement with the theory.

For better understanding of the nature of interactions in the solutions a temperature dependence of D_f and D_s was measured. These investigations revealed that the diffusive mobility of PVP/C_{60} complexes increases with heating (D_f increases) due to the increase of their kinetic energy while the diffusion coefficient D_s decreases (Fig. 8). The decrease of D_s with heating points to an increase of correlation between the scatterers. These data support the supposition that the organization of the solutions of PVP/C_{60} complexes is a consequence of a balance of attractive forces between fullerenes and repulsive forces based on the excluded volume effect of polymeric parts of the complexes. Indeed, the solubility of PVP decreases with temperature leading to a decrease of the repulsive forces and, consequently, to the decrease of the distances between fullerenes (ξ). Presumably the attractive forces increase with the decrease of the distances between fullerenes or, in other words, the correlation in the solution increases with temperature. The shape of the correlation function, shown in Fig. 9, also points to increasing interactions in the solution with temperature (the deviation of the correlation function from the single-exponentiality increases strongly with temperature). However, the intensity of scattered light is almost independent of temperature proving that there is no molecular aggregation in the solution (Fig. 10). The dissymmetry of scattered light does not depend on temperature either. The independence of the intensity of scattered light on temperature is presumably attributed to the compensation of two competitive effects: the increase of concentration fluctuations due to the increase of the kinetic energy of Brownian motion when heated and, on the other hand, the increase of fluctuation hindrance due to the increase of intermolecular correlation. Thus the intensity of scattered light may slightly increase or decrease with temperature according to the shift of the balance of these two effects. Say, at 50 °C the effect of interactions prevail while at 60 °C the balance is shifted towards the first effect (Fig. 10). It was also found that the process of heating is reversible, i.e. the R_h distribution and the value of the intensity return to their initial values when cooling the solution to 20 °C after heating.

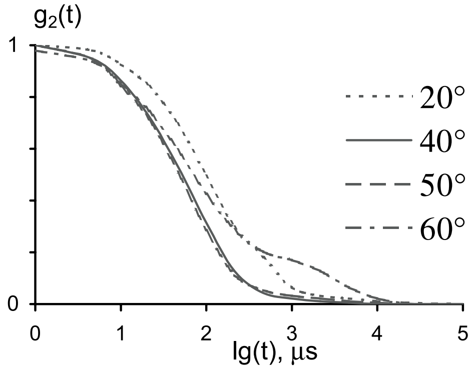

Fig. 9. Temperature dependence of the correlation function for the sample with $M_{PVP} = 10 \times 10^3$ at scattering angle 150°.

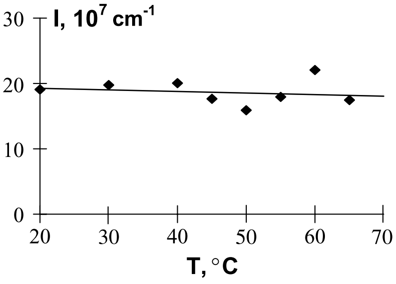

Fig. 10. Temperature dependence of the intensity of scattered light for the sample with $M_{PVP} = 10 \times 10^3$ at scattering angle 150°.

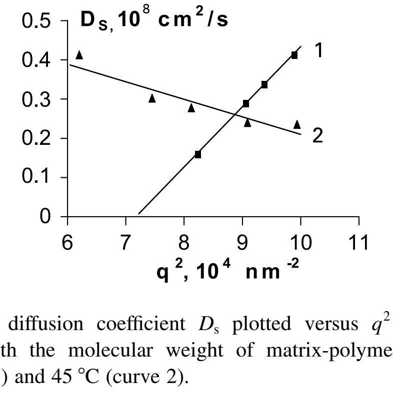

Fig. 11. The diffusion coefficient D_s plotted versus q^2 for PVP/C_{60} complexes with the molecular weight of matrix-polymer 10×10^3 at 20 °C (curve 1) and 45 °C (curve 2).

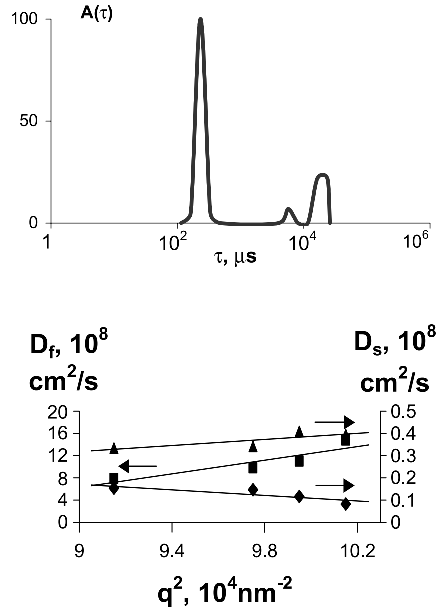

Fig. 12. Spectra of relaxation times obtained by DLS at scattering angle 150° (top) and diffusion coefficients D_f (squares), D_{s1} (triangles), and D_{s2} (diamonds) plotted versus q^2 (bottom) for PVP/C_{60} complexes with the molecular weight of matrix-polymer 10×10^3 at 65 °C.

The change of the slope in the q-dependence of D_s for the sample with $M_{PVP} = 10 \times 10^3$ from positive at 20 °C to negative at 45 °C confirms the assumption of the increase of correlation in the solution with temperature (Fig. 11): the effect of intermolecular interactions becomes stronger than the effect of polydispersity at 45 °C and the q-dependence is mostly determined by interactions at high temperatures. At 65 °C the interactions are so strong that it becomes possible to separate the effects of polydispersity and interactions and three distinct modes are observed in the spectra of relaxation times (Fig. 12). The diffusion coefficients of the first two modes (D_f and D_{s1}) have positive slopes of their q-dependencies and describe the diffusion of the complexes and domains, respectively, while the diffusion coefficient of the third, the slowest mode (D_{s2}) has a negative slope.

4. Conclusions

Static and dynamic light scattering measurements revealed that strong intermolecular interactions with a correlation length of about 45–50 nm are present in dilute aqueous solutions of PVP/C_{60} complexes. The experimental dynamic light scattering results are in good agreement with the theory for systems with strong intermolecular interactions and with the assumption that fluctuation hindrance in the solutions is a consequence of the balance of attractive forces between fullerenes and repulsive forces of an entropic nature between the polymeric parts of the complexes. The question about the nature of the interactions between fullerenes requires further investigations. However, it seems likely that the interactions are of electrostatic nature [14].

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