Effect of Centrifugal Field upon Hydrodynamic Characteristics of Fullerene C$_{60}$ and Poly(N-vinylpyrrolidone) Complex in Aqueous Solutions

Elena Tarabukina[a]; Illia Krasnov[a]; Olga Ratnikova[a]; Elena Melenevskaya[a]; Alexander Filippov[a]

[a] Institute of Macromolecular Compounds, Russian Academy of Sciences, St. Petersburg, Russia

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis
Taylor & Francis Group

Effect of Centrifugal Field upon Hydrodynamic Characteristics of Fullerene C$_{60}$ and Poly(N-vinylpyrrolidone) Complex in Aqueous Solutions

Elena Tarabukina, Illia Krasnov, Olga Ratnikova, Elena Melenevskaya, and Alexander Filippov

Institute of Macromolecular Compounds, Russian Academy of Sciences, St. Petersburg, Russia

Abstract: Velocity ultracentrifugation method was employed to study aqueous solutions of fullerene C$_{60}$ and poly(N-vinylpyrrolidone) complex (PVP-C$_{60}$). Strong dependence of sedimentation coefficient S_0 on ultracentrifuge rotor speed n was found. The S_0 value increases as the value of n decreases from that corresponding to isolated PVP-C$_{60}$ macromolecules to the value that the clusters of PVP-C$_{60}$ (registered by the light-scattering method) would have at $n \to 0$. This dependence indicates that molar mass and size of clusters change depending on the centrifugal field applied.

INTRODUCTION

High biological and antiviral activity of fullerene[1,2] has stimulated many studies of fullerene-containing aqueous solutions. One way to introduce hydrophobic fullerene molecules into water is to prepare complexes of

fullerene with water-soluble polymers. The advantage of such complexes is that the unique electron structure of fullerene is not distorted, since fullerene molecules are combined with the polymer not by covalent but by donor-acceptor bonds.[3–5]

Investigation of fullerene C_{60} and C_{70} complexes with poly(N-vinylpyrrolidone) (PVP) by static (LS) and dynamic (DLS) light-scattering methods revealed that large, relatively stable intermolecular structures, which are referred to as clusters or domains, are formed in their dilute solutions, which can be detected even at very small dilutions.[5–11] Molar masses M_w of clusters obtained by the light-scattering method are one to two orders of magnitude greater than those of matrix polymers used for complex preparation. Cluster molar mass (MM) and size depend on the polymer and solvent nature, fullerene content, fullerene type, and the MM of the polymer. DLS study in dilute regime showed the presence of a slow mode attributed to low-range concentration fluctuations. Intermolecular interactions responsible for this mode were confirmed by its concentration and angular dependence.[7]

Despite the formation of clusters in PVP and C_{60} complex (PVP-C_{60}) solutions having been discovered some time ago, their nature is not completely clear so far. The assumption was put forward that these intermolecular interactions are governed by the balance of the attractive forces of fullerenes and repulsive forces of an entropic nature between PVP chains.[7]

Investigation of the same solutions of PVP-fullerene complexes by the methods of molecular hydrodynamics gave substantially different results. In particular, molar masses M_{SD} obtained by sedimentation and diffusion analysis were close to M_{SD} of the matrix polymer.[6,10,11] Intrinsic viscosity values [η] for the complex and the matrix polymer coincided, and sometimes the same dependencies of the specific viscosity on concentration were obtained.[5,6] In addition, the isothermal translational diffusion coefficient values for polymer-fullerene complexes were close to those for the matrix polymer.[5,12]

DLS as well as LS methods normally imply that during experiments the solution maintains static state, i.e., it is not subjected to external forces. In these terms both LS and DLS methods can be regarded as ''static'' methods. In contrast, methods of molecular hydrodynamics deal with solutions in motion (during the transport of matter). The different results obtained by static and transport methods suggest that intermolecular interactions between macromolecules of the complex inside clusters are quite weak, and clusters seem to be destroyed in hydro-dynamic fields. Translational diffusion experiments carried out at very small osmotic gradients confirm this point of view in qualitative terms. Under these conditions, the presence of clusters in polymer-fullerene complex solutions was identified, which became apparent as the

diffusion boundary dispersion declined from the straight line at high time values.[9–11]

No detailed investigations of the effect of external forces on the cluster organization of fullerene-containing polymer solutions were carried out. However, a study of this kind may be useful in order to understand the nature of intermolecular interactions responsible for polymer-fullerene cluster formation. We think that analytical ultracentrifugation is one of the experimental methods that could be helpful in the study of this problem. The centrifugal force affecting clusters can be changed by varying the rotor speed. In fact, in the course of ultracentrifugation, the centrifugal force affects the dissolved species, thus moving them apart from the rotation center. The rate of particle movement in the centrifugal field is characterized by sedimentation coefficient S. The S value is proportional to molar mass M and inversely proportional to translational friction coefficient f:

$$S \equiv \frac{1}{\omega^2 X} \frac{dX}{dt} = M \frac{(1 - \bar{v}\rho_0)}{N_a f} \tag{1}$$

where $\omega = 2\pi n/60$ is the rotor angular velocity in radians per second (n being the rotor speed in revolutions per minute, rpm), X is the particle coordinate relative to the rotation center, t is the sedimentation time, $\bar{v}$ is the partial specific volume of the solute, ρ_0 is the solvent density, and N_a is Avogadro's number. Since the centrifugal field is radially non-uniform, the points of the sedimenting particle differently distanced from the rotation axis are exposed to unequal centrifugal forces, which can result in particle rotation as well as deformation. Singer[13] calculated these two effects for Gaussian coils and proved theoretically that the resulting small S changes are, as a rule, mutually compensated. However, it was shown later[14–16] that for very large chain molecules possessing high equilibrium rigidity, the effect of the nonuniform centrifugal force can be important in high centrifugal fields.

Whenever it is not a single macromolecule that is of concern, the super-molecular structure sediments. The action of these forces can result in destruction of the super-molecular structure, provided the interactions between the macromolecules are weak enough. For instance, a destruction of this kind was observed for super-molecular structures based on poly(phenylene) derivatives.[17] Apparently, a similar phenomenon can occur for clusters formed in the steady state of a fullerene-polymer complex solution.

A "standard" velocity sedimentation experiment for synthetic polymer study is carried out, as a rule, at the rotor speed $n \geq 40000$ rpm. As mentioned above, at such high speeds, the centrifugal force is strong enough to completely destroy the cluster structure of PVP-C_{60} solutions.

The decrease of n value leads to a decrease of the centrifugal force affecting the sedimenting species, i.e., to a decrease of the deforming and/or destroying action of the centrifugal field. We can expect that at lower n, the clusters will be partly destroyed depending on the centrifugal force. The frictional characteristics and MM are different for clusters at different extents of destruction, hence the $S(n)$ dependence.

The objective of this study was to analyze the rotor speed effect upon hydrodynamic properties and molar mass of PVP and fullerene C_{60} complex in aqueous solutions. Cluster destruction in the solutions was studied using the velocity sedimentation method at different ultracentrifuge rotor speeds, i.e., exposing the cluster to different centrifugal forces. The results obtained in this way were compared with those obtained by the light-scattering method.

MATERIALS AND METHODS

The PVP-C_{60} complex was prepared by the solid-state method[9] by dispersing the crystalline C_{60} and amorphous PVP with the aid of a magnetic stirrer in vacuum (10^{-6} mm Hg). For this purpose, we used fullerene C_{60} (Fullerene Technologies, Ltd., 99.5% grade) and PVP synthesized in the Institute of Macromolecular Compounds, Russian Academy of Sciences (RAS). To extract water-soluble fraction, the product was dissolved in water, and the filtered solution was liophilized. The complex formation was confirmed by the widening of fullerene signal in the nuclear magnetic resonance (NMR) spectrum. The fullerene content in water-soluble fraction was estimated by UV spectroscopy in chloroform solutions of the product, using the extinction of fullerene (wavelength $\lambda = 258$ nm, extinction coefficient $k = 19000$). UV spectra were measured using a Specord M 40 spectrophotometer (Carl Zeiss Jena, Germany). The fullerene content determined by the spectrophotometer was 0.7% mass of the complex. As mentioned above, the complex formation takes place due to the donor-acceptor interaction between carbonyl groups of PVP and fullerene.[5,9] The PVP-C_{60} complex obtained was studied in distilled water (Vecton, Russia), which had the following characteristics at 20.0°C: density $\rho_0 = 0.998$ g/cm^3, viscosity $\eta_0 = 1.005 \times 10^{-2}$ poise, and refractive index $n_0 = 1.333$.

Intrinsic viscosity was measured in an Ostvald viscometer with a flow time of water of 73.5 s at 21.0°C. Intrinsic viscosity value $[\eta]$ and Huggins constant k' were calculated according to the Huggins equation.

Velocity sedimentation analysis was carried out in a MOM 3180 analytical ultracentrifuge (MOM Hungarian Optical Works, Budapest, Hungary) provided with a refractometric optical system at the rotor temperature of 21.0°C. Sedimentation boundary was formed artificially,

stratifying the solvent onto the solution. The solutions studied were in the concentration range of $(0.06–1.0) \times 10^{-2}\,g/cm^3$. Sedimentation diagrams were unimodal and symmetric. The position of the sedimentation peak was taken as the maximum of the sedimentation diagram. Sedimentation coefficients were calculated as $S = \Delta(lnX_{max})/(\omega^2\Delta t)$, X_{max} being the radial coordinate of the sedimentation peak maximum. To discuss the hydrodynamic properties of PVP-C_{60}, the S values obtained were adjusted to 20.0°C using the formula $S_{20} = S_T\left(\frac{(1-\bar{v}\rho_0)_{20}}{(1-\bar{v}\rho_0)_T}\right)\left(\frac{\eta_{0,T}}{\eta_{0,20}}\right)$, where values for water at 20.0°C and at the experimental temperature are denoted by subscripts 20 and T, respectively. The specific partial volume $\bar{v}$ was measured at 21.0°C in a picnometer with the volume $2.036\,cm^3$. The buoyancy $(1 - \bar{v}\rho_0)$ within the temperature interval of $1°$ is mainly defined by ρ_0, which was measured in a picnometer $(\rho_{0,\,21} = 0.998\,g/cm^3)$. The viscosity of water at 21.0°C was controlled by means of the viscometer $(\eta_{0,\,21} = 0.984 \times 10^{-2}$ poise).

Translational diffusion coefficient D was measured in a Tsvetkov optical device based on the Lebedev polarizing interferometer (Institute of Macromolecular Compounds, RAS, Russia).[15,16] The D value was calculated from the dependence slope of the diffusion boundary dispersion on time. The diffusion boundary dispersion was calculated by the area and maximal ordinate method. The measurements were carried out at solution concentration $c = 0.06 \times 10^{-2}\,g/cm^3$. The D value obtained was taken as equal to the diffusion coefficient at infinite dilution D_0. It was assumed that at such small c, the concentration effects can be neglected as those usually obtained for solutions of flexible polymers in the vicinity of zero concentration.[18,19] It should be stressed that the absence of concentration effect at small concentrations had been shown for PVP-fullerene complexes.[11]

MM of the complex was determined in accordance with Svedberg equation:[20]

$$M_{SD} = \frac{S_0}{D_0} \cdot \frac{RT}{1 - \bar{v}\rho_0} \tag{2}$$

T being the absolute temperature, R being the universal gas constant, and S_0 being the sedimentation constant.

Static light scattering was carried out with a Sofica photo goniodiffusiometer (France). Dust was removed from the solution and solvent through Millex (polyvinylidenefluoride (PVDF)) filters with a pore diameter of $0.45\,\mu m$. The wavelength of polarized incident light was $546\,nm$. The instrument was calibrated relative to benzene; the benzene scattered intensity was taken as $R_V = 2.32 \times 10^{-5}\,cm^{-1}$. Exceeding intensity of scattered light I was registered depending on its concentration within the scattering angle range of 45–135°. The results were processed in

accordance with the Zimm method.[18] Weight-average molar mass M_w as well as the radius of gyration R_g for the PVP-C_{60} complex were obtained. The refractive index increment $dn/dc = 0.17\,cm^3/g$ was measured in an IRF-23 refractometer (LOMO, Russia).

RESULTS AND DISCUSSION

The complex of PVP-C_{60} under study was characterized by intrinsic viscosity, diffusion and sedimentation coefficients, hydrodynamic M_{SD} and weight-average M_w molar masses, and the radius of gyration. Intrinsic viscosity and the Huggins constants were $[\eta] = 0.46 \times 10^{-2}\,cm^3/g$ and $k' = 0.5$, respectively. The translational diffusion coefficient was $D = 2.7 \times 10^{-7}\,cm^2/s$. Velocity sedimentation was studied at a rotor speed $n = 40000$ rpm. Figure 1 demonstrates the plot of the dependence of $\Delta ln X_{max}$ on the experiment time Δt characterizing the movement of the sedimentation boundary, for different concentrations of the PVP-C_{60} solution. Figure 2 (line 2) shows the dependence of the reciprocal sedimentation coefficient on concentration. Linear plots of the same kind are typical of dilute polymer solutions. The sedimentation coefficient at infinite dilution $S_0 = 2.3 \times 10^{-13}$ s and the sedimentation concentration coefficient $k_s = 60\,cm^3/g$ were calculated using the equation $1/S = 1/S_0(1/ + k_s c)$.
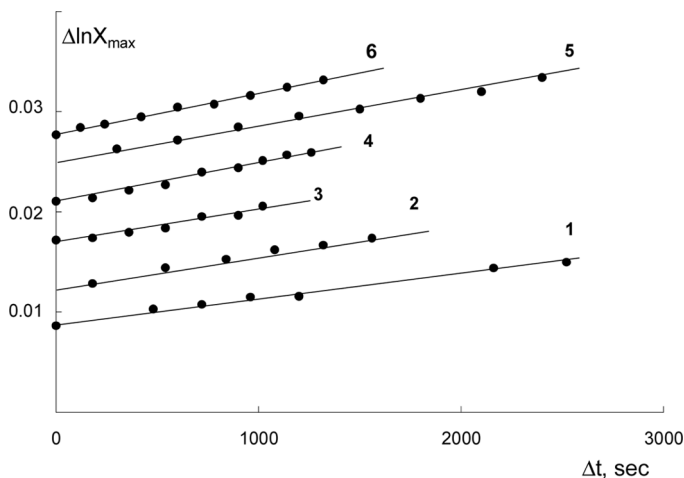

Figure 1. Dependence of $\Delta ln X_{max}$ on Δt obtained at 40000 rpm for PVP-C_{60} aqueous solutions with concentrations of (1) 0.99, (2) 0.47, (3) 0.36, (4) 0.17, (5) 0.1, and (6) $0.07 \times 10^2\,g/cm^3$.
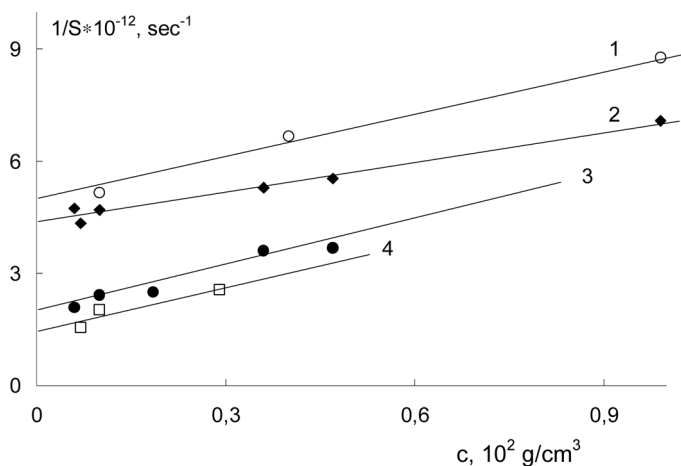
Figure 2. Concentration dependences of reciprocal sedimentation coefficient S^{-1} for aqueous PVP-C$_{60}$ solutions obtained at rotor speeds 55000 (1), 40000 (2), 18000 (3), and 10000 rpm (4).

The $[\eta]$, D, and S_0 values obtained are typical of synthetic polymers. The magnitude of $\bar{v} = 0.80 \, \text{cm}^3/\text{g}$ obtained for PVP-C$_{60}$ is close to that for aqueous PVP solutions.[22] M_{SD} value for the complex was found to be 94000 g/mol. Note that the values of the hydrodynamic invariant

$$A_0 = \eta_0 \left(\frac{D_0}{T}\right)^{2/3} \left[\frac{[\eta]S_0 R}{100(1 - \bar{v}\rho)}\right]^{1/3} \tag{3}$$

and the sedimentation parameter

$$\beta_S = N_A \left[R^{-2}\left(\frac{D_0 \eta_0}{T}\right)^2 \frac{S_0 \eta_0}{1 - \bar{v}\rho} k_s\right]^{1/3} \tag{4}$$

obtained for the complex studied, $A_0 = 3.17 \times 10^{-10} \, \text{erg/grad·mol}^{1/3}$ and $\beta_s = 1.24 \times 10^7 \, \text{mol}^{-1/3}$, correspond to the values for flexible chain polymers[19,23,24]; PVP belongs to this class of polymers.[25] The A_0 and the β_s values were calculated using molecular hydrodynamics data.

On the other hand, the MM of the complex under study obtained by means of the light-scattering method $M_w = 1100000 \, \text{g/mol}$ is an order of magnitude higher than M_{SD}. Thus, the molecular characteristics obtained in the static state (by the light-scattering method) and in the disturbed state (under the exposure to centrifugal field, viscometer shear flow gradient, and osmotic gradient) are substantially different, as well as those found for the fullerene-polymer complex solutions studied previously.[9,11] Therefore, we confirmed once more cluster formation in

PVP-C_{60} water solutions and also registered their destruction in the ultracentrifuge at high rotor speed.

In order to specify the conditions under which intermediate clusters appear between their static and completely destroyed states, the sedimentation of PVP-C_{60} aqueous solutions at different rotor speeds within the interval from $n = 10000$ to 55000 rpm was investigated. Thus, the centrifugal acceleration at the same distance from the axis of rotation, and therefore the force affecting the sedimenting species, increases 30 times.

Figure 3 demonstrates a semilogarithmic dependence of the sedimentation boundary displacement for the PVP-C_{60} solution at $c = 0.1 \times 10^2$ g/cm^3 on the product $\omega^2 t$ for rotor speeds $n = 55, 40, 30, 18,$ and 10×10^3 rpm. Experimental points fit straight lines well, the slopes corresponding exactly to the sedimentation coefficient S (Equation (1)). It can be observed that S values differ noticeably, increasing with a decrease of the ω value. Figure 4 shows the dependence of $\Delta ln X_{max}$ on the experiment time Δt at a small rotor speed $n = 18000$ rpm for PVP-C_{60} solutions of different concentrations. The dependence of S on the concentration obtained from these plots is given in Figure 2 (line 3). Similar to the $S^{-1}(c)$ dependence obtained under "standard" conditions ($n = 40000$ rpm), the dependencies found at different n are well approximated by straight lines (Figure 2). Sedimentation coefficients at infinite dilution S_0 and concentration sedimentation coefficients k_s for different n are given in Table I.
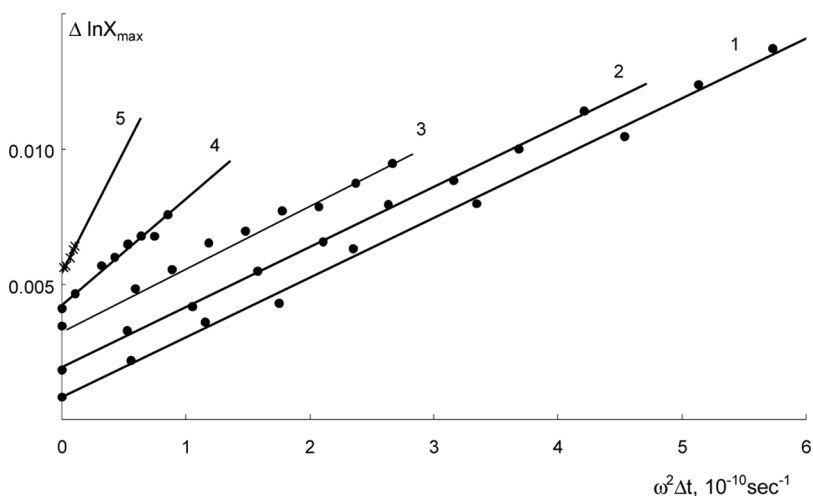

Figure 3. Dependence of $\Delta ln X_{max}$ on $\omega^2 \Delta t$ for PVP-C_{60} solution ($c = 0.1 \times 10^{-2}$ g/cm^3) at rotor speeds 55000 (1), 40000 (2), 30000 (3), 18000 (4), and 10000 rpm (5).
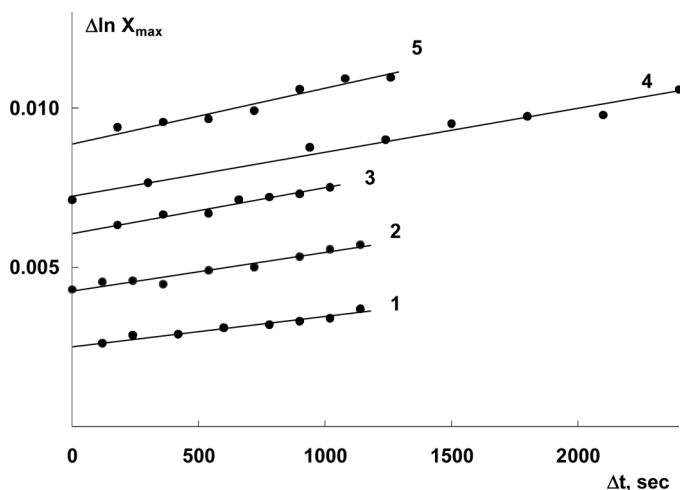
Figure 4. Dependence of $\Delta ln X_{max}$ on Δt obtained at 18000 rpm for PVP-C_{60} aqueous solutions with concentrations of (1) 0.47, (2) 0.36, (3) 0.18, (4) 0.1, and (5) 0.07×10^2 g/cm^3.

It can clearly be seen from Table I as well as in Figure 5, where the dependence of S_0 on n is shown, that with a decrease in rotor speed, the sedimentation coefficient value increases monotonically. The change in S_0 is rather high, the S_0 value increasing more than three times with n changing from 40000 and 55000 rpm to 10000 rpm.

It is worth it to mention that the S dependence on n may be due to different reasons, the first of which is the high hydrostatic pressure in the sedimentation cell, and hence, the change of solvent properties. This effect is usually taken into account by means of the corresponding corrections or by extrapolating the S values to a meniscus position where the hydrostatic pressure is close to 0.[18,20,26,27] Although water is a low compressible liquid compared to organic solvents, the pressure may noticeably affect the value of S,[28] and it would be useful to extrapolate the S values obtained at high n to the meniscus position. However, the extrapolation was unreliable, since the artificial sedimentation boundary was formed far from the meniscus, and the extrapolation range was much larger than the sedimentation peak displacement. Therefore, the comparison was made of the complex under study with pure PVP sedimentation. No $S(n)$ dependence for pure PVP aqueous solutions was found. For example, the values of $S = 2.4 \times 10^{-13}$ s at $n = 55000$ rpm and $S = 2.5 \times 10^{-13}$ s at $n = 18000$ rpm were obtained for the PVP sample with $M_{SD} = 180000$ g/mol at solution concentration $c = 0.07 \times 10^2$ g/cm^3. This suggests that the change of hydrostatic pressure in the sedimentation

Table I. Hydrodynamic and molecular characteristics of PVP-C$_{60}$ in aqueous solutions obtained at different ultracentrifuge rotor speeds and in static state

n, rpm	$S_0 \times 10^{13}$, s	$k_s \times 10^{-2}$, cm^3/g	$M_w \times 10^{-4}$, g/mol	$M_{SD} \times 10^{-4}$, g/mol	$M_{KS} \times 10^{-4}$, g/mol	$M_s \times 10^{-4c}$, g/mol			r_h^d, nm			
						M_1	M_2	M_3	$r_{h(ks)}$	r_{h1}	r_{h2}	r_{h3}
0	9.2^a	—	110	—	—	—	—	—		50^b		
10000	6.9	2.7	—	—	98	95	62	114	27	27	17	32
18000	5.4	2.2	—	—	62	53	40	65	22	19	14	23
30000	2.6	—	—	—	—	9.5	9	12	—	7	7	9
40000	2.2	0.6	—	9.4	8.8	6.7	6.7	9.2	8	6	6	8
55000	2.0	0.9	—	8.8	8.6	5.2	5.4	7.1	8	5	5	7

^{a}S$_0$ calculated using M$_w$ and the equation $S_0 = 8.81 \times 10^{-3} M^{0.5}$. [37]

^{b}r$_g$.

^{c}M$_1$, M$_2$, M$_3$ were calculated using S$_0$ and the equations $S_0 = K \cdot M^{1-b}$ from the articles[25],[37],[36] respectively.

^{d}r$_{h(ks)}$, r$_{h1}$, r$_{h2}$, and r$_{h3}$ were calculated from the M$_{ks}$, M$_1$, M$_2$, and M$_3$ values respectively and Equation (8).
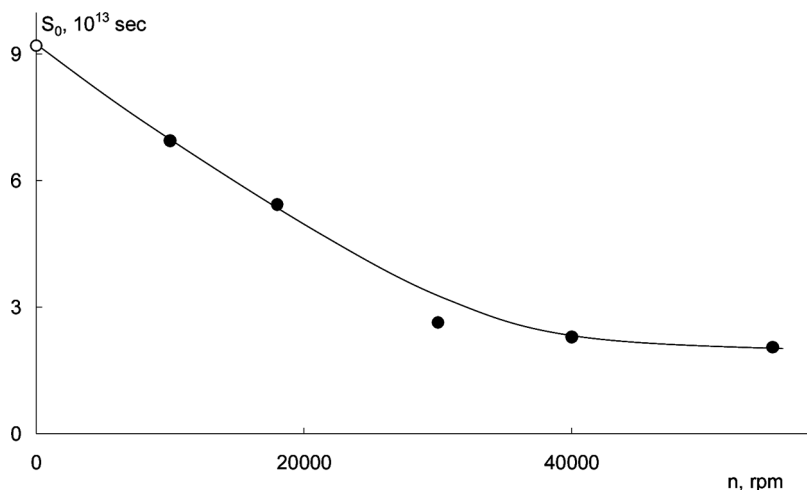
Figure 5. Experimental dependence of sedimentation coefficient S_0 upon rotor speed for PVP-C_{60} aqueous solution (solid points); S_0 value at $n = 0$ (open point) was obtained from the equation $S_0 = 8.81 \times 10^{-16} \cdot M^{0.5}$ [37] using the M_w value. Line is provided to guide the eye.

cell does not directly influence the sedimentation coefficient of the PVP-C_{60} aqueous solution.

The $S(n)$ dependence not related to the hydrodynamic pressure was observed for different "polymer-solvent" systems close to θ-point.[29] In this case, S value decreased as n magnitude increased. The effect disappeared when the thermodynamic quality of the solvent improved (temperature was changed). Water is thermodynamically a good solvent for PVP-C_{60} complex, since the second virial coefficient A_2 is positive at the temperature of the measurements, and all experiments were carried out at temperatures remote from θ. Far away from θ-point, the change of the thermodynamic quality of the solvent due to pressure in the sedimentation cell may lead to dependence of the concentration coefficient k_s upon n.[30] Note that in both cases cited,[29,30] the concentration dependence of S weakened (k_s values decreased) if n decreased.

As mentioned above, the $S(n)$ dependence may occur also for very large macromolecules. The effects were observed experimentally by many authors.[16,31,32] However, as a rule, the change in S with centrifugal field described in the cited papers did not exceed 20–50% within the n range from 10000 to 55000 rpm. The effect observed in the current work was much higher. The explanation of the $S(n)$ dependence observed may be as follows. At rest, PVP-C_{60} macromolecules are self-organized in

clusters, which are destroyed in the nonuniform centrifugal field; the higher the rotor speed, the higher the degree of cluster destruction. Thus, the sedimenting species, that is, clusters of PVP-C_{60}, are different at different n values; they have different MM and size (therefore different friction coefficients), hence the different S_0 (see Equation (1)). We suggest that the $S(n)$ dependence reflects different extents of cluster destruction in the centrifugal field.

Let us analyze this point of view by comparing the results obtained with the data for sedimentation of PVP solutions available in the literature. Examine the k_s values obtained for the studied solutions in relation to S_0; k_s is known to be a function of specific volume V of the sedimenting particle $k_s = \Lambda N_a / MV$, parameter Λ being dependent on the model that is used to describe the particle hydrodynamic and thermodynamic properties.[33,34] If the Mark-Kuhn-Houwink-Sakurada equation

$$S_0 = KM^{1-b} \tag{5}$$

is valid for the homological set, then k_s may be described as[35]

$$k_s = \gamma_s S_0^{(3b-1)/(1-b)} \tag{6}$$

where γ_s is a parameter depending on the thermodynamic and hydrodynamic interactions in the "polymer-solvent" system. The superscript $1-b$ of Equation (5) is determined by the conformation of the macromolecule, its size, and the thermodynamic quality of the solvent.[19] Table I shows simultaneous increase of k_s and S_0 values for the PVP-C_{60} complex solutions with a decrease of the n value. In other words, the k_s behavior differs from the cited dependences of $k_s(S_0)$ caused by the change of the solvent thermodynamic quality.[29,30] The experimental points obtained for PVP-C_{60} at different n are in surprising agreement with the data obtained by different authors for homological sets of PVP in aqueous solutions (Figure 6).[25,36,37] The superscript $(3b-1)/(1-b)$ of Equation (6) for the PVP-C_{60} complex becomes 1.1–1.5 according to our estimation. Supposing that Equations (5) and (6) are both true for PVP-C_{60}, we can estimate superscript $1-b = (0.45-0.50)$ for Equation (5). Such an order of $1-b$ magnitudes is characteristic of flexible chain polymers [18], hence hydrodynamic properties of the PVP-C_{60} complex in clusters are similar to those of flexible chain macromolecules in good solvents.

On this basis, it was possible to evaluate the MM of the PVP-C_{60} complex at different rotor speeds by taking the equations that are true for PVP homologues obtained by various researchers.[25,36,37] The equations used for the calculations are given in Table II, which also shows the intervals of MM and sedimentation constant S_0. It is
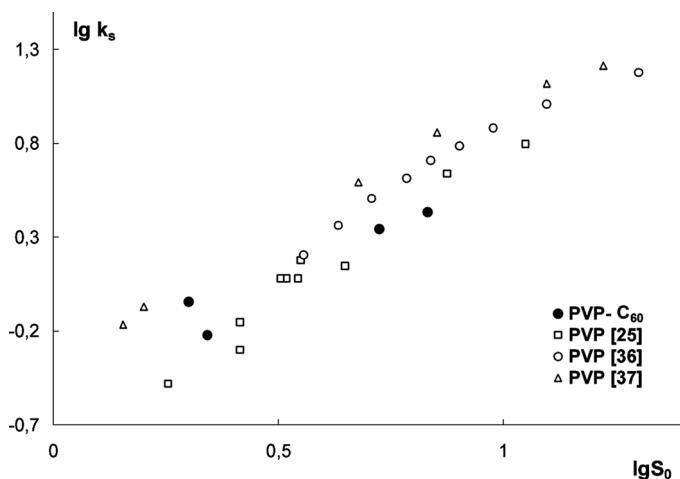
Figure 6. Logarithmic dependence of concentration coefficient k_s vs. sedimentation coefficient at infinite dilution S_0 for PVP-C_{60} and PVP[25,36,37] aqueous solutions.

significant that all the mentioned relations were obtained for rather wide MM and, correspondingly, S_0 ranges.

In addition, molar masses of the PVP-C_{60} complex M_{ks} were calculated with use of the equation combining experimental values of S_0 and concentration coefficient k_s[24,38–40]:

$$M_{ks} = (N_a/\beta_s)^{3/2}[S_0\eta_0/(1 - \bar{v}\rho_0)]^{3/2}k_s^{1/2} \qquad (7)$$

The expression (7) contains parameter β_s, which is invariant for different "polymer-solvent" systems with respect to MM and the structure of the repeated unit. It was mentioned above that the value of parameter β_s obtained for the PVP-C_{60} complex aqueous solutions at high rotor speed is in agreement with the average β_s value for flexible chain polymers in thermodynamically good solvents. The M_{ks} magnitudes of the PVP-C_{60} complex corresponding to different n were calculated assuming β_s that value does not change at different rotor speeds.

MM of clusters ($M_{[1]}$, $M_{[2]}$, $M_{[3]}$) calculated by means of different equations from Table II and M_{ks} found for different n are given in Table I. In spite of some differences in their values calculated in different ways, they show a certain conformity, and also the tendency for MM to increase with rotor deceleration up to M_w value measured by light-scattering method at the static state of the solution (i.e., at $n{\to}0$).

In Table II, an equation is given that describes the $k_s(S_0)$ dependence obtained for PVP-C_{60} aqueous solution shown in Figure 5. The obtained

Table II. Equations $k_s = \gamma_s\, S_0^{(3b-1)/(1-b)}$ and $S_0 = KM^{1-b}$ for PVP according to the data of different authors and for PVP-C$_{60}$ aqueous solutions

Polymer (reference)	Solvent	$M \times 10^{-4}$, g/mol	$S_0 \times 10^{13}$, s	$k_s = \gamma_s\, S_0^{(3b-1)/(1-b)}$	$S_0 = KM^{1-b}$
PVP ([25])	Water/0.1 M AcNa	4–229	0.7–11.2	$K_s = 15.3 \cdot S_0^{1.61}$	$S_0 = 2.14 \times 10^{-2} \cdot M^{0.42}$
PVP ([36])	Water	25–730	3.6–20.0	$k_s = 0.25 \cdot S_0^{1.5}$	$S_0 = 1.5 \times 10^{-2} \cdot M^{0.44}$
PVP ([37])	Water/0.2 M NaCl	1.2–242	1.43–16.7	$k_s = 0.46 S_0^{1.32}$	$S_0 = 8.81 \times 10^{-3} \cdot M^{0.5}$
PVP-C$_{60}$	Water	—	2.1–6.9	$k_s = 0.36 S_0^{1.3}$	—

expression seems to fit best the equation from Tarabukina[36] where the subscript $1 - b = 0.5$. That is why the formula of the type (3) from Tarabukina[36] was taken into account to estimate the S_0 value a cluster would have at zero rotor speed ($n{\to}0$). In this case, M_w value for PVP-C_{60} complex was used.

The $S_0(n{\to}0)$ value is shown in Figure 5. It can be seen that the sedimentation coefficient decreases four times from $S_0 = 9, 2 \times 10^{-13}$ s to $S_0 = (2, 1 \pm 0, 1) \times 10^{-13}$ s while the rotor speed increases from 0 to 55000 rpm. Its value becomes practically constant at $n > 30000$ rpm. Thus, the S_0 value decreases from the value that would be expected for a cluster (at $n{\to}0$) to the value corresponding to the sedimentation of an isolated PVP-C_{60} complex macromolecule (at high n).

The radius of an equivalent hydrodynamic sphere r_h for the PVP-C_{60} complex can be estimated using the obtained data. The friction coefficient of a spherical particle is described by the Stokes formula $f = 6\pi\eta_0 r_h$. Taking into account Equation (1), we get:

$$r_h = \frac{M(1 - \bar{v}\rho_0)}{6\pi\eta_0 S_0 N_a} \tag{8}$$

r_h values were calculated using different types of MM shown in Table I. For high n, the values of M_{SD} were used, and for $n{\to}0$ the r_g value was obtained from the light-scattering data. It can be seen from Table I that r_h values for the PVP-C_{60} complex calculated with different formulas are in good agreement for the same n. On the other hand, r_h increases to approach r_g value for the unperturbed condition of clusters at $n{\to}0$. Different r_h values for the PVP-C_{60} complex are assumed to correspond to different degrees of destruction of the PVP-C_{60} clusters.

CONCLUSION

PVP-C_{60} complex aqueous solutions were studied by the methods of molecular hydrodynamics. The dependence of sedimentation velocity of these solutions on the ultracentrifuge rotor speed was found. It was shown that sedimentation velocity of PVP-C_{60} reflects different extents of macromolecular self-assembly into clusters, depending on the effect of the centrifugal force.

The results show that the super-molecular structure of fullerene-polymer complexes in solutions can be observed and investigated using the sedimentation velocity method. The experimental data obtained by this method are in agreement with light-scattering results. The study of fullerene-polymer complex behavior under external force effect makes it possible to analyze the change in cluster structure of PVP-C_{60} complex solutions.

REFERENCES

[1] Friedman, S. H., P. S. Ganapathi, Y. Rubin, and G. L. Kenyon. (1998). Optimizing the binding of fullerene inhibitors of the HIV-1 protease through predicted increases in hydrophobic desolvation. *J. Med. Chem.* **41**(13), 2424.

[2] Da Ros, T. and M. Prato. (1999). Medical chemistry with fullerenes and fullerene derivatives. *Chem. Commun.* **8**, 63.

[3] Khairullin, I. I., Y.-H. Chen, and L.-P. Hwang. (1997). Evidence for electron charge transfer in the PVP-C_{60} systems as seen from ESR spectra. *Chem. Phys. Lett.* **275**, 1.

[4] Chen, Y.-H., I. I. Khairullin, M.-P. Suen, and L.-P. Hwang. (1999). Electron spin resonance and infrared spectroscopy study of the polyvinylpyrrolidone-C_{60} composite. *Fullerene Sci. Technol.* **7**(5), 807.

[5] Vinogradova, L. V., E. Yu. Melenevskaya, A. S. Khachaturov, E. E. Kever, L. S. Litvinova, A. V. Novokreshchenova, M. A. Sushko, S. I. Klenin, and V. N. Zgonnik. (1998). Water-soluble complexes of C_{60} fullerene with poly(N-vinylpyrrolidone). *Polym. Sci. A* **40**(11), 1152.

[6] Sushko, M. L., I. A. Baranovskaya, E. N. Bykova, and S. I. Klenin. (2001). Light scattering of aqueous solutions of fullerene-containing polymers. *J. Mol. Liq.* **91**, 59.

[7] Sushko, M. L., H. Tenhu, and S. I. Klenin. 2002. Static and dynamic light scattering study of strong intermolecular interactions in aqueous solutions of PVP-C_{60} complexes. *Polymer* **43**(9), 2769.

[8] Tarassova, E., V. Aseev, H. Tenhu, and S. Klenin. (2003). Poly(vinyl pyrrolidone)–C_{70} complexes in aqueous solutions. *Polymer* **44**, 4863.

[9] Ratnikova, O. V., E. V. Tarasova, E. Yu. Melenevskaya, V. N. Zgonnik, I. A. Baranovskaya, and S. I. Klenin. (2004). Behavior of poly-N-vinylpyrrolidone–fullerene C_{60} composites in aqueous solutions. *Polym. Sci. A* **46**(7), 752.

[10] Klenin, S. I., M. L. Sushko, M. A. Dumpis, L. I. Pozniakova, and L. B. Piotrovskii. (2000). Light scattering in aqueous solutions of fullerene containing polymers. *J. Tech. Phys.* **70** (3), 27 (in Russian).

[11] Tarasova, E. V.(2006). Dynamic and static light scattering and the properties of fullerene–polymer complexes and fullerene containing polymers in solutions. Ph.D. diss, St. Petersburg State University (in Russian).

[12] Melenevskaya, E. Yu., O. V. Ratnikova, N. P. Yevlampieva, I. I. Zaitseva, V. T. Lebedev, D. N. Orlova, M. V. Mokeev, A. S. Khachaturov, and V. N. Zgonnik. (2003). Fullerene-containing poly(N-vinylpyrrolidone) complexes synthesized in the presence of tetraphenylporphyrin. *Polym. Sci. A* **45**(7), 1091.

[13] Singer, S. (1947). Effect of centrifugal field on resistance to motion of thread-like molecules in solution. *J. Polym. Sci.* **2**, 290.

[14] Budtov, V. P. (1969). Effect of macromolecules velocity on the coefficient of translational friction. *Vestnik LGU* **3**, 58 (in Russian).

[15] Zimm, B. H. (1974). Anomalies in sedimentation. IV:Decrease in sedimentation coefficients of chains at high fields. *Biophys. Chem.* **11**, 279.

[16] Zimm, B. H., V. N. Schumaker, and C. B. Zimm. (1976). Anomalies in sedimentation. V:Chains at high fields, practical consequences. *Biophys. Chem.* **5**, 265.

[17] Schnablegger, H., M. Antonietti, C. Göltner, J. Hartmann, H. Cölfen, P. Samori, J. P. Rabe, H. Häger, and W. Heitz. (1999). Morphological characterization of the molecular superstructure of polyphenylene derivatives. *J. Colloid Interface Sci.* **212**, 24.

[18] (a) Tsvetkov, V. N., V. E. Eskin, and S. Ya. Frenkel. (1964). *The Structure of Macromolecules in Solution*. Moscow: Nauka (in Russian); (b) Cwetkow, W. N., W. Je. Eskin, and S. Ja. Frenkel. (1968). *Structura macroczasteczek w roztworach*. Warszawa: Wydawnistwa naukowo-techniczne.

[19] Tsvetkov, V. N. (1989). *Rigid-Chain Polymers*. New York: Plenum.

[20] Fujita, H. (1975). *Foundations of Centrifugal Analysis*. New York: Wiley Intersci. Publ.

[21] Eskin, V. E. (1986). *Light Scattering by Polymer Solutions*. Leningrad: Nauka (in Russian).

[22] Polymer Handbook, (1999). 4th ed. ed. J. Brandrupt, E. H. Immergut, and E. A. Grulke. New York: John Wiley.

[23] Tsvetkov, V. N., P. N. Lavrenko, and S. V. Bushin. (1982). Hydrodynamic invariant of polymer molecules. *Russ. Chem. Rev.* **51**(10), 975.

[24] Pavlov, G. M. and S. Ya. Frenkel. (1988). The sedimentation parameter of linear polymer molecules in absence of excluded volume effects. *Acta Polym.* **39**(3), 107.

[25] Pavlov, G. M., E. F. Panarin, E. V. Korneeva, K. V. Kurochkin, V. E. Baikov, and V. N. Ushakova. (1990). Hydrodynamic properties of polyvinylpyrrolidone molecules from the data of sedimentation-diffusion analysis and viscometry. *Polym. Sci. A* **32**(6), 1190.

[26] Blair, J. E. and J. W. Williams. (1964). The sedimentation velocity experiment and the determination of MW distributions. *J. Phys. Chem.* **68**, 161.

[27] Dishon, M., M. T. Stroot, G. H. Weiss, and D. A. Yphantis. (1971). New approach to the effects of pressure dependence on sedimentation velocity experiments. *J. Polym. Sci. Polym. Phys.* **9**(5), 939.

[28] Schuck, P. (2004). A model for sedimentation in inhomogeneous media. II:Compressibility of aqueous and organic solvents. *Biophys. Chem.* **108**, 201.

[29] Jacob, M., R. Varoqui, S. Klenine, and M. Daune. (1962). Mesures de diffusion de translation et de sedimentation de chaines macromoleculaires en solvant Θ:Effets de la concentration et de la vitesse. *J. Chim Phys.* **59**, 866.

[30] Cherkasov, A. N., T. N. Osipova, and S. I. Klenin. (1968). Investigation of diffusion and sedimentation of grafted macromolecules in solution. *Polym. Sci. A* **10**, 1348 (in Russian).

[31] Levin, D. and F. Hutchinson. (1973). Neutral sucrose sedimentation of very large DNA from Bacillus subtilis. *J. Mol. Biol.* **75**(3), 455.

[32] Eigner, J., C. Schildkraft, and P. Doty. (1962). Concentration effects in the hydrodynamic properties of deoxyribonucleic acid. *Biochim. Biophys. Acta* **55**, 13.

[33] Pyin, C. W. and M. Fixman. (1964). Friction coefficient of the polymer molecules in solution. *J. Chem. Phys.* **41**(4), 937.

[34] Imai, S. (1969). Concentration dependency of the sedimentation coefficient. *J. Chem. Phys.* **50**(5), 2116.

[35] Pavlov, G. M. and S. Ya. Frenkel. (1982). Concentration dependence of the sedimentation coefficient of macromolecules. *Polym. Sci. B* **24**(3), 178 (in Russian).

[36] Tarabukina, E. B. (1992). Molecular characteristics of semi-rigid chain polymer determination by means of the velocity ultracentrifugation without using other methods. Ph.D. diss., Leningrad, Institute of Macromolecular Compounds, RAS (in Russian).

[37] Sholtan, W. (1952). Molekulargewichtsbestimmung von polyvinylpyrrolidon mittels der ultrazentrifuge. *Makromol. Chem.* **7**, 209.

[38] Pavlov, G. M. and S. Ya. Frenkel. (1983). The sedimentation of diluted and semi-diluted solutions of cellulose nitrate. *Polym. Sci. A* **25**(5), 1015 (in Russian).

[39] Pavlov, G. M. and S. Ya. Frenkel. (1986). Determination of molecular weight of linear polymer using concentration dependence of sedimentation coefficient. *Polym. Sci. B* **28**(5), 353.

[40] Pavlov, G. M., E. B. Tarabukina, and S. Ya. Frenkel. (1995). Self-sufficiency of velocity sedimentation for the determination of molecular characteristics of linear polymers. *Polymer* **36**(10), 2043.