

Formation of Fullerene Clusters in Carbon Disulfide: Data on Small-Angle Neutron Scattering and Molecular Dynamics

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Abstract—Fullerene solutions in carbon disulfide are studied by small-angle neutron scattering (SANS). In addition to earlier experiments on the given system, the range of measured transmitted impulses is extended and the influence of solution preparation methods on C₆₀ cluster formation in these solutions is studied. It is shown that the formation of large C₆₀ clusters (with a size of about 10 nm) is due to nonequilibrium methods of solution preparation. For nonequilibrium dissolution, there is a 10% excess of the observed fullerene size in the solution over the calculated value. It has been established by simulation of the C₆₀/CS₂ interface by molecular dynamics methods that inclusion of how solvent molecules are organized on the C₆₀ surface leads to a decrease in the fullerene size in the solution, observed by using SANS. In this paper, the effect of excess R_g is explained by the presence of small clusters in the solution (approximately 10% of dissolved C₆₀ molecules). It is discovered that there is a time variation in the concentration of the saturated solution. The explanation of this effect using a model of formation and sedimentation of large clusters (with a size of 100 nm or more) is proposed.

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INTRODUCTION

Fullerenes (one of the allotropic forms of carbon) were discovered at the end of the last century [1] and have attracted large interest from the point of view of fundamental and applied research. Promising practical applications of fullerene (for example, in biomedicine) are related to the use of various C₆₀ solutions. C₆₀ solutions in which the saturation concentrations of a large number of various solvents were determined were first studied in [2–4]. In contrast to other forms of carbon (graphite and diamond), fullerenes dissolve sufficiently well in organic, weakly polar, and nonpolar solvents (the concentrations are ~1–10 mg/ml); but they dissolve badly in polar solvents (<0.01 mg/ml) and are insoluble in water.

Fullerenes in some solutions exhibit a variety of interesting properties, such as solvatochromism [5], an anomalous temperature dependence of solubility [6], and a nonlinear concentration dependence of third-order optical susceptibility [7]. Some of these effects can be explained by the formation of clusters from C₆₀ molecules in fullerene solutions. Evidence on the existence of clusters in various C₆₀ solutions was given in [5, 8–12]. A qualitative explanation for the anomalous

dependence of solubility using a model of C₆₀ cluster formation, growth, and dissolution in solutions was proposed in [3]. The authors of [3] used a phenomenological drop model. A theory of crystallosolvate dissolution in C₆₀ solutions was proposed later [4, 14–15], and the effect of an anomalous dependence of solubility was described quantitatively using this theory.

In this paper, we use small-angle neutron scattering (SANS) to study the fullerene solution in carbon disulfide. It should be mentioned that the dimensions of C₆₀ macromolecules are close to the resolution limit of this experimental method. C₆₀ solutions in carbon disulfide (CS₂) are of special interest for studies using SANS. As was shown in [16], carbon disulfide is the most appropriate fullerene solvent for this method. This is due to the comparatively high contrast between solvent and particles, to the high solubility of C₆₀ in CS₂ (compared with that of other compounds), and the low coherent background (compared with that of other solvents) predominantly determined by the hydrogen content in the compound. The first experiments using SANS for C₆₀/CS₂ solutions were performed successively by the Affholter group in 1993 [16]. A series of SANS experiments on C₆₀/CS₂ solutions was performed later [17–19]. The scattering vector q ranging from 0.05 to 0.4 Å⁻¹

(the dimensions of detected particles were $\sim 20\text{--}200$ Å) was measured in these studies. The authors of all these papers have pointed out that they did not discover fullerene clusters with dimensions in the above-mentioned range in the solutions under study up to the saturation concentration. Later, the authors of [20] performed an experiment in which they studied C_{60}/CS_2 solutions with various concentrations using electron microscopy and positron spectroscopy. They observed the cluster state in the solutions under study. C_{60} aggregates exist in solutions with concentrations ranging from ~ 0.02 mg/ml to the saturation concentration. The dimensions of the observed particles ranged from 100 to 500 nm; in this case, it is important to note that the majority of fullerene in the C_{60}/CS_2 solution are in the form of clusters.

In this paper, we study C_{60}/CS_2 solutions using SANS measurements in an extended range of scattering vectors q in order to verify the presence of large clusters in the system. Our results agree with the results of earlier SANS experiments (in the range $q > 0.05$ Å⁻¹). However, the measurements for smaller q revealed the presence of a small concentration of clusters with dimensions of ~ 120 Å in the solution. Such clusters are formed in solutions prepared either under the action of ultrasound or as a result of a continuous stirring (non-equilibrium preparation methods), and they do not form if the solution is prepared without any external influence. It was shown for both cases that the measured gyration radius R_g of particles inertia in solution is more than 10% of the calculated one for the C_{60} molecule. This result cannot be explained by either a statistical measurement error or a Guinier approximation error; i.e., an interesting effect is observed in this case, and it must be studied and explained. These results are discussed using nucleation theory. We conclude that the experimental data can be described qualitatively using a limited-growth model. We also discuss whether large clusters described in [20] can be formed.

The results of SANS experiments are compared to those of simulation of the C_{60}/CS_2 solution by the molecular dynamics method. We discuss an interesting property of fullerene solutions in carbon disulfide detected using the simulation, namely, specific ordering of solvent molecules near the fullerene molecule surface (the short-range order). This effect leads to the presence of an excluded volume around the C_{60} molecule.

We also revealed in our experiments that there is a time variation in the concentration of the saturated C_{60} solution. We propose an explanation for this effect and consider the corresponding model [21] of formation and sedimentation of large clusters (with dimensions of 100 nm or more) not observed in SANS experiments.

SAMPLE PREPARATION

In this paper, we used C_{60} fullerene of 99.5% purity (Fullerene Technologies, St. Petersburg) and carbon disulfide CS_2 of 99.98% purity (KhimMed, Moscow). The C_{60} fullerene solutions in carbon disulfide were obtained using two different procedures. Following the fullerene dissolution methods described in [2, 16, 18], the first series of samples was prepared using powerful ultrasound. After C_{60} was added to carbon disulfide, a cell was placed in an ultrasonic bath until fullerene was completely dissolved (the duration of this process was several minutes). As a result, the solution acquired the violet tint usual for C_{60}/CS_2 [2, 16]. The samples prepared according to the described procedure are called samples of type A in what follows. The solutions of two concentrations, 3.9 and 7.6 mg/ml, were prepared. The second concentration is close to the saturation concentration of fullerene in carbon disulfide [2–4].

The solutions of the second series (samples of type B) were prepared in such a way that all possible external influence was excluded. The duration of the dissolution of fullerene in disulfide was about 2 days under these conditions. The dissolution process can be observed; namely, the number of C_{60} crystals on the bottom of a vessel decreases with time. Samples of type B with two concentrations of 4 and 7.9 mg/ml were studied in our experiments.

SANS EXPERIMENTS

The data on neutron scattering were obtained using a YuMO small-angle diffractometer located at the IBR-2 pulse reactor operating in the Frank Laboratory of Neutron Physics of the Joint Institute for Nuclear Research (Dubna) and using a YS (Yellow Submarine) small-angle diffractometer located at the stationary reactor operating in the Budapest Neutron Center (BNC, Hungary).

We measured the isotropic differential cross section of scattering per unit volume (the scattering intensity in what follows) as a function of the absolute value of the scattering vector $q = (4\pi/\lambda)\sin(\theta/2)$, where λ is the neutron wavelength and θ is the scattering angle. The neutron wavelength in the interval 0.05–0.5 nm (λ was determined by the time-of-flight method) and a sample-detector distance of 13 m (the detector size was 0.45 m) were used to obtain the range of q equal to 0.2–0.4 nm⁻¹ in the case of the YuMO diffractometer [22]. The data were calibrated according to the standard procedure using vanadium. A fixed wavelength of 0.386 nm (the monochromatism $\Delta\lambda/\lambda = 13\%$) and sample-detector distances of 1.3 and 5.6 m (the detector size was 0.64 m) were used in the BNC experimental setup. This choice of parameters makes it possible to record data in the range $q = 0.1\text{--}4.0$ nm⁻¹. Calibration using a millimeter water layer was performed after the subtraction of the background and after the corrections for a buffer and scattering by the cell. The YuMO diffractometer

was used for experiments on samples of type A, and the YS diffractometer (BNC), on samples of type B.

The processing of experimental data includes (1) the use of the Guinier approximation to determine the gyration radius of particles in the solution and (2) comparison of the experimental scattering curves with the calculated ones for various models. The use of the Guinier approximation for the experimental data is valid in the range of scattering vectors q for which the relation $qR_g \ll 1$ holds. In this case, the approximation is given by

$$I(q) = I(0)\exp(-(qR_g)^2/3), \quad (1)$$

where $I(0)$ is the intensity of scattering into a zero angle and R_g is the gyration radius of a particle in the solution. If there are particles with different dimensions in the solution, this quantity determines the average value.

For the case in which C_{60} in the solution is in the form of free molecules, the scattering curve is described by

$$I(q) = n\Delta\rho^2V^2\Phi^2(qr_{C_{60}}), \quad (2)$$

where $\Phi(qr_{C_{60}})$ is the form factor of the C_{60} molecule, $\Delta\rho = (\bar{\rho} - \rho_s)$ is the difference between the average scattering length density of fullerene and the scattering length density of the solution, V is the volume of the C_{60} molecule, and n is the fullerene bulk concentration in the solution.

If clusters are formed in the solution, their contribution to scattering must be taken into account in the expression for the scattering intensity. For this, we use the function of the size distribution $D_N(R)$ of clusters:

$$I(q) = n\int\Delta\rho^2V^2D_N(R)\Phi^2(qR)dR. \quad (3)$$

where $\Phi(qR)$ is the form factor of the fullerene cluster of radius R . Comparing the experimental data with the curve obtained using (2), we can determine whether the cluster is in the solution. The subsequent simulation of scattering curves using (3) allows obtaining the calculated size distribution of clusters.

RESULTS AND DISCUSSION

The scattering curves for samples of type A were obtained by SANS and are shown in Fig. 1. These data are temperature-independent in the range of 288 to 315 K. The deviation of the experimental data from the calculated curves of scattering by the C_{60} molecular solution (relation (2)) in the range $q < 0.06 \text{ \AA}^{-1}$ demonstrates that there are clusters of radius $r > 50 \text{ \AA}$ in the solution. The function of the size distribution of C_{60} clusters can be determined (Fig. 2) from the fitting of the experimental data (formula (3)). The resulting function $D_N(R)$ is temperature-independent and is the same for both concentrations (3.9 and 7.6 mg/ml) of the solution. As can be seen from Fig. 2, the main fraction of fullerene in the solution is in the form of free molecules

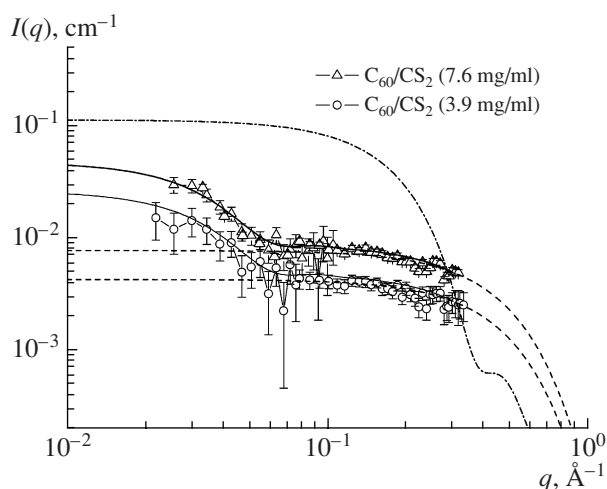


Fig. 1. Graphs of the neutron scattering intensity for two concentrations of samples of type A. The dashed lines correspond to the calculated curves of scattering by fullerene molecular solutions with the corresponding concentrations. Solid lines correspond to the fitting of the experimental data to the model curves for the solution containing C_{60} clusters. The dot-and-dash line corresponds to the calculated scattering intensity as a function of the size distribution of clusters given in [3].

and the concentration of clusters is small (the ratio of the concentration of fullerene in the molecular form to that in the cluster composition is 300 : 1).

The scattering curves shown in Fig. 3 were obtained for two different concentrations of samples of type B. All measurements were conducted at room temperature. There is no sharp discrepancy with the model scattering curves for monomers in the case of samples of type B. However, the calculation using the Guinier approximation for these solutions (Fig. 4) yields a greater gyration radius ($3.84 \pm 0.18 \text{ \AA}$) of the particles in the solution than the calculated one (3.57 \AA [16]).

The function $p(r)$ of the distribution over the distances was also obtained using the inverse Fourier transform. This function for two concentrations of the C_{60}/CS_2 solution is shown in Fig. 5, where it is compared with the calculated function for the fullerene molecule.

An interesting effect observed in the SANS experiments was a continuous decrease in the concentrations of the C_{60}/CS_2 solutions (samples of type B) over the course of 2 days. The rate of this decrease was very small; the concentrations of the solutions decreased by 5–10% during the experiment. This result can be compared with the data in [23], in which this effect was studied using UV/VIS spectroscopy for C_{60} and C_{70} solutions in carbon disulfide CS_2 .

We now discuss the effect of large cluster formation in the C_{60}/CS_2 solution, discovered using SANS and electron microscopy.

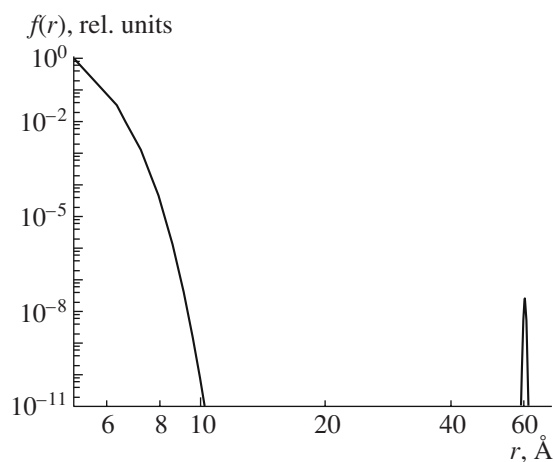


Fig. 2. Function of the size distribution of clusters in the C_{60}/CS_2 solution obtained from the fitting of the experimental data using formula (3).

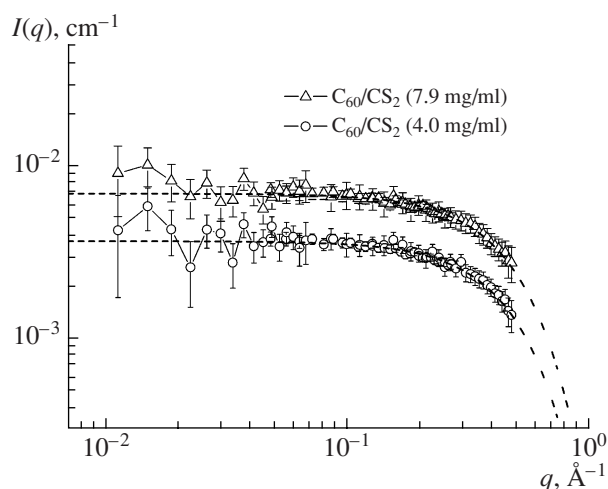


Fig. 3. Experimental SANS data (BNC) for C_{60}/CS_2 solutions; samples of type B. The dashed line corresponds to the calculated curves for scattering by fullerene molecular solutions in carbon disulfide with the corresponding concentrations.

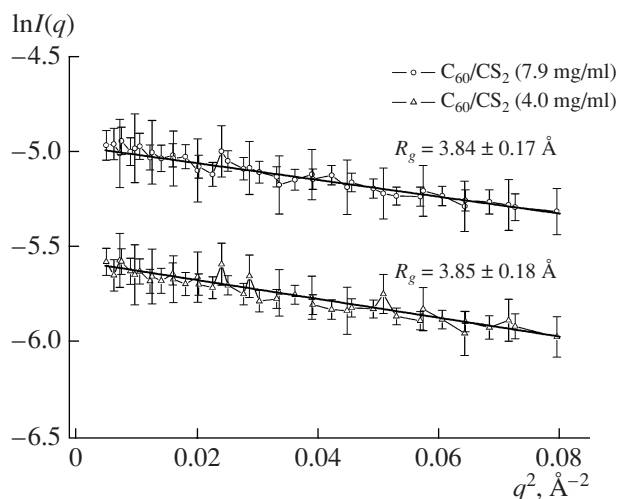


Fig. 4. Guinier approximation of the data obtained for samples of type B.

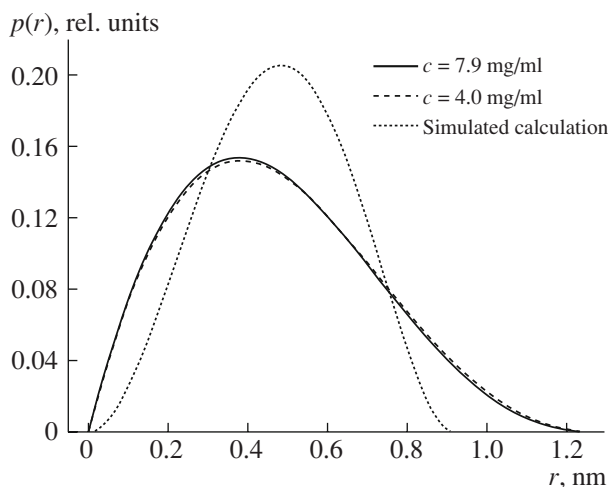


Fig. 5. Function $p(r)$ for two concentrations of the fullerene solution compared with the calculated curve for the fullerene molecule.

SANS experiments revealed the presence of large aggregates in the solution only for samples of type A. The size distribution of particles is independent of the solution concentration or temperature for the values used. It is important to note that our data agree completely with the data obtained in the previous papers [16–19]. Large deviations of the curve from the model one are observed for the molecular C_{60} solution in the range $q < 0.06 \text{ \AA}^{-1}$, while the effect of large clusters is not observed for large values of q used in the previous papers. The large-cluster formation and the size distribution of large clusters can be explained qualitatively in the framework of nucleation theory [24, 25]. The application of nucleation theory to the fullerene solutions under study was described in [26, 27]. The most appropri-

ate model for the cluster state obtained in our experiments (Fig. 2) is the limited-growth model, in which a term corresponding to either a certain interaction between solution particles or some other effect limiting cluster growth is added to the expression describing the cluster formation. Thus, a concentration of clusters with a certain average size is formed in the system.

Comparing the results of the measurements on the C_{60}/CS_2 solutions prepared using ultrasound and stirring [28, 29] or under equilibrium conditions, we can conclude that formation and growth of large clusters in the solution is due to the nonequilibrium effect on the system during the fullerene dissolution process. If the solution is prepared without such effects, then stable large clusters are not formed.

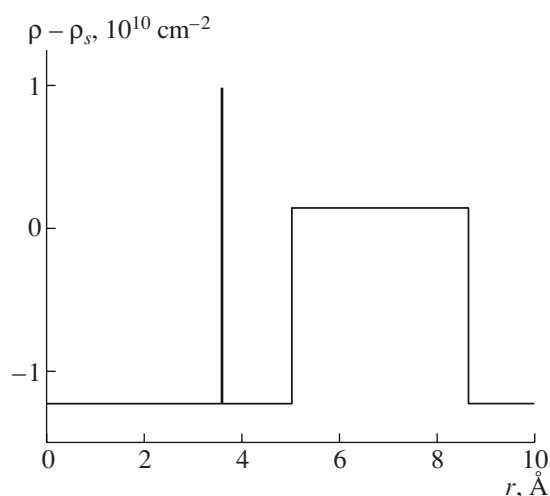


Fig. 6. Calculated profile of the neutron scattering length density for scattering by a $\text{C}_{60} \cdot 24 [\text{CS}_2]$ solvate [17].

The reasons for the formation of clusters studied in [20] can also be treated using nucleation theory. The evaporation of a drop of solution on a substrate is a necessary part of the method according to the preparation procedure described in [20]. During evaporation, the fullerene molecules in the drop of solution are under strongly nonequilibrium conditions; namely, the concentration of the solution exceeds the saturation concentration by a great deal and continues to increase (up to infinity in the general case). Under such conditions, exotic structures can form, such as fractal clusters observed by high-resolution electron microscopy [20].

The second interesting effect observed using SANS involves the value of the gyration radius R_g of particles in the $\text{C}_{60}/\text{CS}_2$ solution. This value exceeds the calculated gyration radius of the fullerene molecule by $\sim 10\text{--}15\%$. In one of the previous papers describing SANS experiments, this effect was explained by the solvation of C_{60} molecules in the solution [17]. The authors of [17] obtained the nonzero second virial coefficient A_2 characterizing the interaction between the solvent molecules and molecules of dissolved material [30]. Later, the authors of [18] conducted repeated measurements and collated the data given in all previous papers describing SANS experiments [16, 18, 19]. As a result, it was shown that the interaction of CS_2 and C_{60} molecules in the solution can be neglected. In our paper, we also verify this assumption, comparing the simulated scattering intensity for the $\text{C}_{60} \cdot 24 [\text{CS}_2]$ solvate with the experimental one. For the solvate model described in [17], the profile of the density of the neutron scattering length is shown in Fig. 6. A comparison of the calculated curve $I(q)$ with the results of the SANS experiments on samples of type B (the concentration is 7.9 mg/ml) is shown in Fig. 7. The calculated gyration radius of the solvated C_{60} molecule is 3.98 \AA . This value is greater than the experimental value, which demonstrates that

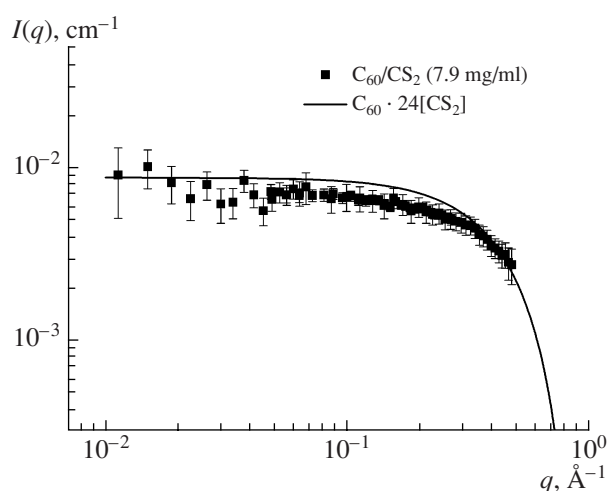


Fig. 7. Comparison of the calculated intensity of scattering by $\text{C}_{60} \cdot 24 [\text{CS}_2]$ solvate with the SANS curves for samples of type B with a concentration of 7.9 mg/ml.

there are no C_{60} solvates in the fullerene solution in carbon disulfide.

In [31], the $\text{C}_{60}/\text{CS}_2$ solution was simulated by molecular dynamics methods. One of the results of this paper is the calculated profile of the bulk concentration of the solvent molecules near the surface of the fullerene molecule. Using these data, we obtained the calculated profile of the scattering length density (Fig. 8). As can be seen, the solvent molecules are ordered near the C_{60} surface, which leads to the existence of an excluded volume around the molecule. It can be expected that the inclusion of this effect in calculating the fullerene gyration radius results in an excessive value corresponding to the experimental results. To verify this hypothesis, we calculate the intensity of neutron scattering for the simulated profile of the scattering length density (Fig. 9) and compare this intensity with the results of the SANS experiments (Fig. 10). As a result, it turns out that the excluded-volume effect cannot be a reason for the excessive R_g of the particle in the solution.

Our calculations revealed an interesting property of the system; namely, the increase in particle size due to the addition of low-contrast components at a remote distance from the particle center leads to a decrease in R_g . This result is not surprising if it is analyzed using the expression for the particle gyration radius [30]:

$$R_g^2 = \frac{\int_V \rho(\mathbf{r}) r^2 dr}{\int_V \rho(\mathbf{r}) dr}. \quad (4)$$

We assume that the reason for excess R_g is the presence of a certain concentration of small C_{60} clusters in the solution. Fractions of dimers (clusters consisting of two fullerene molecules), trimers (clusters consisting of three C_{60} molecules), etc., in the solution lead to the excessive gyration radius.

It is possible to estimate fractions of small clusters in the solution if the following equation is used:

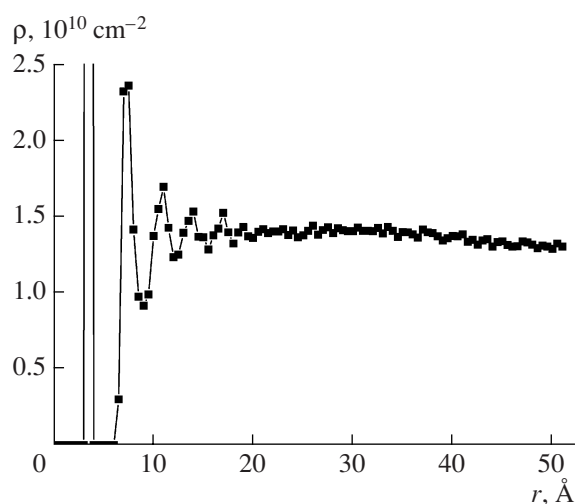


Fig. 8. Profile of the neutron scattering length density for scattering by a single C_{60} molecule according to the molecular dynamics data [31].

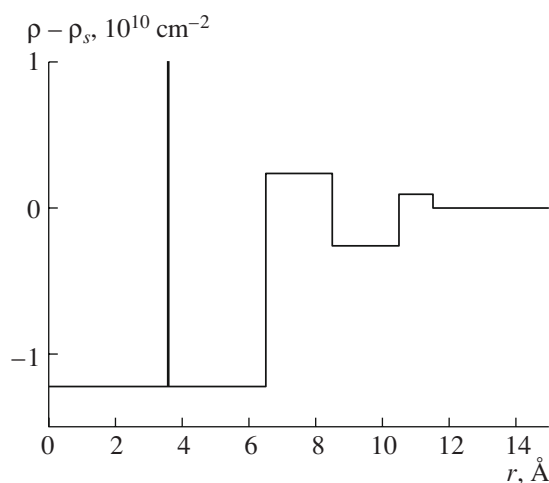


Fig. 9. Simulated profile of the neutron scattering length density for scattering by a fullerene molecule.

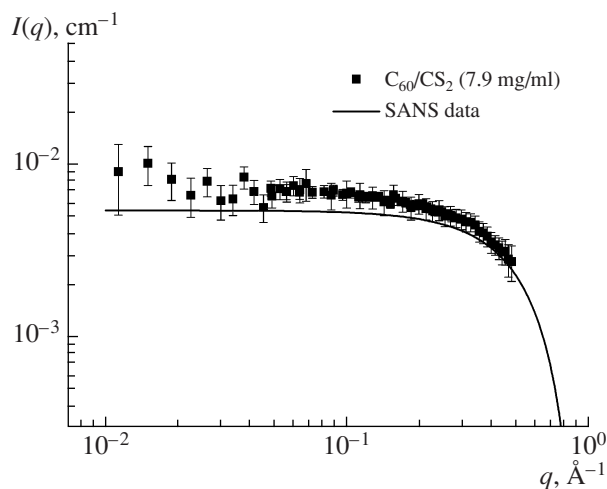


Fig. 10. Comparison of the molecular dynamics results [31] with the SANS data.

$$R_g^2 = R_g^{\prime 2} + \frac{2\alpha}{1 + \alpha} R^2, \quad (5)$$

where α is the relative fraction of C_{60} molecules in the dimer composition, R_g^{\prime} is the gyration radius of a single fullerene molecule, and R is the Van der Waals molecule radius. Formula (5) is valid for the case in which fullerene in the solution exists only in the form of monomers and dimers. Using (5), we obtain the estimate of the concentration of small clusters in the solution. For $R_g = (3.84 \pm 0.18 \text{ \AA})$ obtained using the SANS data, we find that 8.5% of C_{60} molecules exist in the form of small clusters. It is possible to describe this effect more precisely; however, it is sufficient to have Eq. (5) in order to conclude that the presence of small clusters is the most probable reason for excess R_g of the particle in the C_{60}/CS_2 solution.

Using nucleation theory and the hypothesis on cluster formation and growth in the C_{60}/CS_2 solution, it is also possible to explain the above-mentioned effect of the decrease in the concentrations of fullerene solutions with time, which was observed in the measurements using SANS and UV/VIS spectroscopy [23]. To explain the effect of the nonmonotonous time dependence of the solution concentration, we assume that the formation, growth, and sedimentation of large fullerene clusters are possible in the saturated C_{60}/CS_2 solutions. The dimensions of such clusters can be more than 100 nm according to the model, and these clusters cannot be discovered using SANS.

The concentration of the solution is given by

$$c(t) = \sum_{n=1}^{n_{\max}} n f(n, t), \quad (6)$$

where $f(n, t)$ is the bulk concentration of clusters consisting of n C_{60} molecules in the solution at the instant t . During dissolution, large fullerene clusters form in the system; they precipitate slowly with time, decreasing the total concentration of the solution. The ratio of the rates of C_{60} molecule transition from the solid phase to the solution, of cluster growth, and sedimentation determines the possibility that such an effect occurs in the system. The proposed model and results obtained using it were discussed in more detail in [21].

CONCLUSIONS

In this paper, we present the results of the SANS experiments on the fullerene solution in carbon disulfide. For the first set of samples prepared by dissolving C_{60} by means of ultrasound, we have shown that there is a small concentration of clusters with dimensions on the order of 60 \AA in the solution. In this case, we have qualitatively explained the observed cluster state in the framework of the limited-growth model of nucleation theory [26]. We have shown that the reason for the formation of such clusters in the system is the nonequilib-

rium effect on the solution during preparation. If there is no external influence during the process of fullerene dissolution in the carbon disulfide, large clusters are not formed. It is important to note that this result agrees completely with the results of the previous SANS experiments [16–19] and contradicts the data given in [20]. As in the previous papers describing SANS experiments, we have found that the gyration radius R_g ($3.84 \pm 0.18 \text{ \AA}$) of particles in the solution exceeds the calculated value (3.57 \AA [16]) by $\sim 10\text{--}15\%$. It is impossible to explain this effect by either the formation of C_{60} solvates [17] or the excluded-volume effect. We have explained the excessive R_g by the presence of small clusters in the solution, namely, dimers, trimers, etc. Estimation of the fraction of fullerene in the form of clusters yields a value on the order of 10%. In the SANS experiments, we have discovered that the concentration of the saturated solution varies with time. We have proposed the explanation of this effect and considered the corresponding model [21] of formation and sedimentation of large (more than 100 nm) clusters not observed in the SANS experiments.

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