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Formation of C₆₀ Fullerene Clusters in Nitrogen-Containing Solvents

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Abstract—An approach to the description of the growth of C₆₀ fullerene clusters in nitrogen-containing solvents has been proposed within the framework of the nucleation theory. A temporal solvatochromic effect and reorganization of fullerene clusters have been considered upon addition of water to the C₆₀/N-methyl-2-pyrrolidone (NMP) system. In particular, the reorganization of fullerene clusters manifests itself as a sharp increase in the small-angle neutron scattering intensity for cluster sizes of the order of 10 nm. The conclusion has been drawn that, in order to explain these effects, it is necessary to take into account the formation of new (hypothetically, donor–acceptor) bonds between the C₆₀ and NMP molecules with time after the dissolution of fullerene.

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1. INTRODUCTION

An active investigation of C₆₀ fullerene solutions in nitrogen-containing solvents (pyridine, N-methyl-2-pyrrolidone (NMP), and acetonitrile) is associated with a number of interesting effects. These systems are characterized by the formation of clusters of fullerene molecules [1–8], so that this process occurs for a month after the dissolution. This allows one to thoroughly study the processes proceeding in the system at different aggregation stages. One of the most interesting phenomena revealed in these systems is a temporal solvatochromic effect, i.e., a variation in the absorption spectrum of ultraviolet and visible (UV–Vis) radiation with time [2, 3, 5], which correlates with the appearance of large (up to 500 nm in size according to the dynamic scattering data) clusters of fullerene molecules in the system. It should be noted that, despite these large cluster sizes, the system remains stable (i.e., the precipitation of fullerene is not observed). Until now, the mechanism of stabilization of these clusters is not completely understood. One more interesting effect, which in our opinion is associated with the above effect, is the reorganization of clusters when water is added to the C₆₀/NMP system. This effect manifests itself as a sharp increase (at a volume content of water >40% in the final solution) in the small-angle neutron scattering intensity in the momentum transfer range from 0.1 to 0.5 nm^{–1}, which

indicates the destruction of large clusters and the appearance of clusters with characteristic sizes between 10 and 100 nm [6]. This effect is also accompanied by the solvatochromic effect.

The purpose of this work was to analyze the possibility of theoretically describing the effects under consideration in terms of the nucleation theory [9]. This approach was used in our earlier works [10–12] for describing low-polarity solutions of C₆₀ fullerene (in particular, in carbon disulfide). We described the formation of some amount of stable clusters under non-equilibrium conditions, with the cluster size considerably smaller (up to 10 nm) than that observed in systems with nitrogen-containing solvents (medium-polarity solvents). For equilibrium dissolution, the addition of the precipitation of large clusters made it possible to qualitatively reproduce the experimentally observed nonmonotonic dependence of the saturation concentration of the solution on the time.

2. RESULTS AND DISCUSSION

Within the framework of the nucleation theory, the description of the kinetics of cluster formation in C₆₀ solutions is based on the solution to the system of kinetic equations

$$\frac{\partial f(n, t')}{\partial t'} = \left(\frac{c}{c_{eq}^{(\infty)}} \right) \left\{ (n-1)^{1/3} f(n-1, t') + n^{1/3} f(n+1, t') \exp \left[\frac{\Delta G(n+1) - \Delta G(n)}{k_B T} \right] \right\} - \left(\frac{c}{c_{eq}^{(\infty)}} \right) \left\{ (n-1)^{1/3} \exp \left[\frac{\Delta G(n) - \Delta G(n-1)}{k_B T} \right] + n^{1/3} \right\} f(n, t'), \quad (1)$$

where $f(n, t)$ is the time evolution of the distribution function of clusters over sizes (over aggregation numbers n), $\Delta G(n)$ is the work of cluster formation from n monomers in the solution, c is the concentration of the dissolved fullerene (the number of particles per unit volume), and $c_{eq}^{(\infty)}$ is the effective concentration above which the cluster formation begins [10–12]. Let us consider the specific features of the solution to this system of equations for medium-polarity solvents with respect to two effects, i.e., the temporal solvatochromic effect and the reorganization of clusters in C_{60} /NMP solutions upon their dilution with water.

According to the discussions in the literature, the following factors can be responsible for the temporal solvatochromic effect: (1) an increase in the contribution of the light scattering from the clusters formed in the solution, (2) the formation of new bonds between the fullerene molecules in the clusters, and (3) the for-

mation of new bonds between the C_{60} and NMP molecules (mechanism of the donor–acceptor bonds).

Earlier, we established [13] that the growing size of clusters causes a little effect on the absorption spectrum in the UV–Vis range. Therefore, the scattering from clusters cannot explain the solvatochromic effect observed.

If the main contribution to the temporal solvatochromic effect is made by the formation of new bonds of the C_{60} – C_{60} type in the process of the appearance and growth of fullerene clusters, the question arises as to the reason for the stabilization of the cluster size. As in the case of solutions in low-polarity solvents, let us consider the stage of the independent growth of clusters (Fig. 1) in terms of the nucleation theory, which can reflect the quasi-stationary cluster state of the solution [10]. For this purpose, it is necessary that the duration of this stage should correspond to a characteristic time interval during which stable clusters are observed (of the order of a year). The calculation of the clusters lifetime at the independent growth stage for low-polarity solutions of the C_{60} fullerene was performed within the droplet model [10], when the following condition is satisfied:

$$\Delta G(n) = -n\Delta\mu + \alpha_2 n^{2/3}, \quad (2)$$

where $\Delta\mu$ and α_2 are the volume and surface factors, respectively. Correspondingly, the calculation yields the lifetimes of the order of 1 μ s. Similar calculations performed for medium-polarity solutions give times of ~ 10 – 10^3 μ s, which corresponds to smaller values of the saturation concentration and the diffusion coefficient (by one or two orders of magnitude) [14]. As in the case of the low-polarity solvents, this time appears to be insufficient for providing an explanation for the stable state of the clusters, so that an additional mechanism of the cluster stabilization should be introduced into the model. In terms of the nucleation theory (which was also demonstrated for the low-polarity solvents [10]), this can be carried out by modifying expression (1) for the work done to form a cluster; that is,

$$\Delta G(n) = -n\Delta\mu + \alpha_2 n^{2/3} + kn^\beta, \quad (3)$$

where the third term with the empirically chosen parameters k and β is responsible for some interaction in the system, which limits the growth of clusters. The model that uses expression (3) was referred to as the “limited growth model”. However, unlike the low-

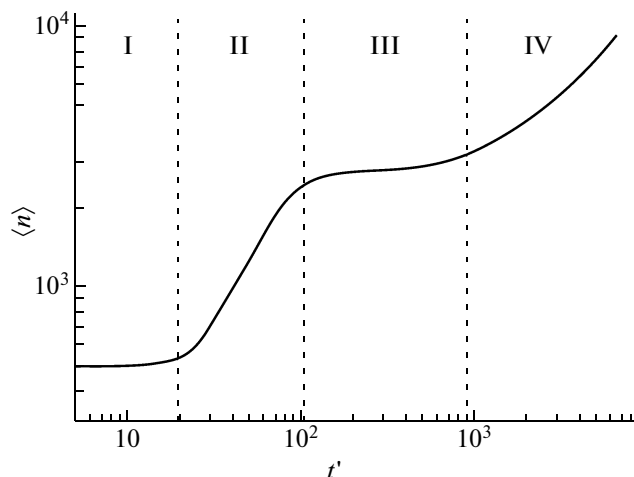


Fig. 1. Characteristic dependence of the average cluster size in the system on the time in terms of the nucleation theory (the dimensionless conventional time is plotted along the abscissa axis [9]). Stage I corresponds to a “delay” determined by the average time of the probabilistic formation of a stable nucleus. Stage II is the steady-state nucleation (an increase in the concentration of clusters capable of growing to a macroscopic size). Stage III is the stage of the independent growth (the competition in the growth of the formed clusters). Stage IV is the Ostwald ripening when one macroscopic cluster is dominant and the solution undergoes phase separation. Stage III corresponds to a quasi-stationary state of the system, which can be interpreted as a stable cluster state for a sufficient time interval.

polarity solutions, a rather large cluster size considerably complicates the solution to Eq. (1) directly for the case of medium-polarity solutions. The aggregate number of particles in the C₆₀ clusters in these systems is approximately equal to 10⁸, in contrast to ~10³–10⁴ for the clusters in the low-polarity solutions. In this case, the numerical solution to the kinetic equations (taking into account the enumeration of the parameters required within the model) becomes impossible in practice. We relate the prospects for the model described here to the possibilities of obtaining the time dependence of the concentration of monomers in the solution $f(1, t)$ from the experiment. On the one hand, this will substantially simplify the solution to the system of equations for large clusters. On the other hand, the experimental dependence $f(1, t)$ can be analyzed and compared with different models. Data on the experimental dependence $f(1, t)$ can be obtained experimentally using an additional optical solvent (for example, hexane), which dissolves the fullerene, on the one hand, and does not mix with the NMP solvent, on the other hand. When this solvent is added to the NMP solutions of the fullerene, the extraction of the fullerene occurs, with the fullerene extracted only in the monomer form [7]. Therefore, by measuring the fullerene concentration in hexane, one can evaluate the concentration of monomers in the NMP solvent.

As can be seen, the limited growth model is incapable of directly answering the question about the reason for the cluster stabilization. Chemically, new bonds are required in order to form an effective stabilizing shell around the clusters. These bonds can be donor–acceptor bonds between the C₆₀ and NMP molecules, and the formation of these bonds is favored by the presence of a nitrogen atom in the ring structure of the molecule of the solvent [3]. An assumption can be made that the competition between the formation of the C₆₀ clusters and the formation of the C₆₀–NMP complexes leads to the limitation of the aggregate growth. Consequently, these bonds can be responsible for the occurrence of the temporal solvatochromic effect.

In our opinion, important information on the mechanism of cluster stabilization is involved in the cluster reorganization effect in the C₆₀/NMP solutions upon dilution with water [6]. An interesting feature of this reorganization is its criticality; i.e., when an abrupt jump in the decreasing size of the cluster is observed upon the addition of water (more than 40 vol % in terms of the final solution). As was demonstrated in [5, 7], this decrease occurs via the detachment of individual monomers from the cluster. This gives reason to suggest that we are dealing with a simple concentration effect occurring in the system upon the dilution, which, nonetheless, should exhibit a critical behavior at a certain concentration. In order to rule out the possibility of this effect, we considered the model system with a maximum size of the fullerene cluster contain-

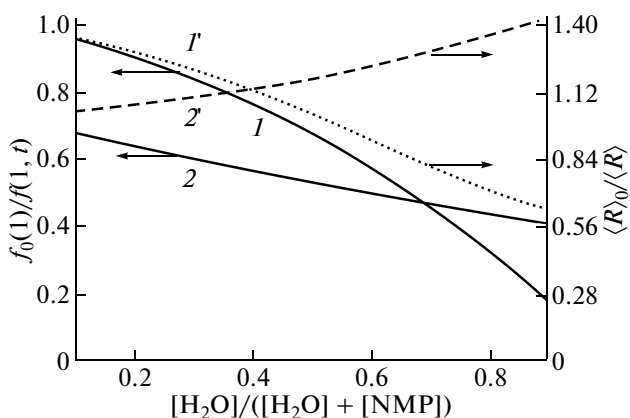


Fig. 2. Model calculations of the dilution of the C₆₀/NMP solution with (1, 1') NMP or (2, 2') water in different proportions within the framework of the nucleation theory. Dependences of (1, 2) the relative change in the monomer concentration and (1', 2') the average cluster size on the volume fraction of the component added to the solution.

ing 10³–10⁴ molecules (~10 nm). It was noted above that the limited growth model can be applied to this system. We analyzed two cases: (1) the dilution was provided by changing the concentration of the clusters in the system and the saturation concentration (the dilution with NMP) and (2) in addition to the previous conditions, the dilution was also accompanied by changing the thermodynamic parameters of the solution toward those of high-polarity systems (the dilution with water). The results of the calculation are presented in Fig. 2. It can be seen that the dilution of the system can lead to a decrease (case 1) and an increase (case 2) in the average cluster size. However, the main result of this study is the absence of the critical behavior in the dynamics of the average cluster size upon the dilution of the system. Therefore, in order to explain this effect, it is also necessary to simulate the interaction of cluster monomers with the solvent.

3. CONCLUSIONS

By analogy with low-polarity solvents, the formation of C₆₀ fullerene clusters in the nitrogen-containing NMP solvent (medium-polarity solvent) has been considered in terms of the nucleation theory. It has been demonstrated that, similarly to the case of low-polarity solvents, in order to explain the stabilization of the cluster size in the NMP solvent, it is necessary to invoke the limited growth model, which corresponds to the formation of an effective stabilizing shell around the clusters. The most probable mechanism of the formation of this shell is associated with the formation of C₆₀–NMP donor–acceptor complexes with time after the dissolution, which gradually limits the growth of clusters.

The nucleation theory has also been applied to assess the concentration effects occurring in the system upon dilution with the NMP solvent or water. It has been demonstrated that the critical changes experimentally observed in the solution upon dilution with water cannot be described by the change in the concentration and thermodynamic characteristics of the system.

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