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KINETICS OF CLUSTER GROWTH
IN POLAR SOLUTIONS OF FULLERENE:
EXPERIMENTAL AND THEORETICAL STUDY
OF C_{60}/NMP SOLUTION

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Кинетика роста кластеров фуллерена в полярных растворах:
экспериментальное и теоретическое исследование раствора C_{60}/НМП

Представлены теоретические модели для описания кинетики роста кластеров фуллерена в растворах C_{60} в N-метил-2-пирролидоне (НМП). Сделан подробный обзор текущего состояния в экспериментальных исследованиях раствора C_{60}/НМП. Обсуждается связь между образованием комплексов C_{60}–НМП, ростом кластеров C_{60} и их влиянием на сольватохромизм. Предложенный теоретический подход к описанию роста кластеров основан на кинетических уравнениях сегрегации частиц. Две развиваемые в работе модели подразумевают модификацию базового подхода. В первой модели рассматривается рост кластеров в пересыщенном растворе C_{60}, ограничиваемый постепенным образованием новых комплексов. Во второй модели рассматривается двухступенчатый процесс: образование комплексов и рост кластеров. Раствор комплексов C_{60}–НМП пересыщен (комплексы агрегируют между собой), в то время как «свободные» молекулы C_{60} не образуют кластеров. Для каждой модели предложена процедура оценки параметров в применении к исследуемым системам.

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Kinetics of Cluster Growth in Polar Solutions of Fullerene:
Experimental and Theoretical Study of C_{60}/NMP Solution

Theoretical models for describing the kinetics of fullerene cluster growth in C_{60} solutions in N-methyl-2-pyrrolidone (NMP) are presented. First, a detailed review of current state of experimental investigation of C_{60}/NMP is given. The relation between C_{60}–NMP complex formation, cluster growth and their impact on solvatochromism is discussed. Next, we propose a theoretical approach for description of cluster growth based on kinetic equations of segregation. Two modifications of basic approach are given. First one treats cluster growth in a supersaturated solution of C_{60}, where new complex formation eventually limits growth of aggregates. In the second model a two-step process of cluster growth is considered: complex formation and cluster growth. The solution of C_{60}–NMP complexes is supersaturated, while initial, «free» C_{60} does not aggregate. For each model a procedure for obtaining parameters is proposed and the parameters values are obtained.

1. INTRODUCTION

Solutions of fullerene C_{60}, a new allotropic form of carbon [1], attract much attention because of their perspective biomedical applications [2]. Additional pure scientific interest also exists — a number of peculiar effects in fullerene solutions has been observed and is being actively investigated. One can mention anomalous solubility dependence on temperature [3], large third-order nonlinear optical response of C_{60} [4], solvatochromic effects [5, 6] and cluster formation [7–11] in solutions. Fullerene molecule itself presents an interesting object for theoretical and experimental study — a highly symmetrical quasispherical particle with the size of 1 nm and a tendency to cluster formation in some solutions.

Unlike graphite and diamond, fullerenes dissolve well in a number of solvents, including organic and polar liquids [12–14]. The range of concentrations obtained varies from very low values, like < 0.01 mg/ml in hexane up to ~ 30 mg/ml in 1,2-dichlorbenzene. There is no single parameter or property of a liquid that can be used to predict fullerene solubility [12, 15, 16]. A general tendency can be emphasized: fullerenes solve well in organic and nonpolar liquids (e.g., benzene, toluene, carbon disulfide), solve weakly in polar solvents (certain alcohols), and do not solve in high-polar liquids. The last class includes water, where C_{60} solubility is reported to be less than $1.3 \cdot 10^{-11}$ mg/ml [17–18].

With respect to cluster growth, fullerene solutions can be classified similarly [19]. Carefully prepared C_{60} solutions in nonpolar liquids are stable molecular solutions of purple color. A certain concentration of clusters can be detected if the solution is oversaturated or prepared in a nonequilibrium way [18, 19]. These clusters have been reported to be as dense as solid fullerite [20], or may have a weak fractal structure [7, 21]. On the other hand, in polar solutions, fullerenes tend to slowly form large stable clusters with sizes above 100 nm [5, 8, 9, 22]. A peculiar transition from initially molecular C_{60} solution of purple color to a brown colored stable colloidal solution is observed. As a general rule, this effect takes place in liquids with the value of dielectric permittivity above 13 [8]. Finally, high-polar fullerene solutions in water can be prepared using certain procedures that include solvent replacement by powerful ultrasonication [23] or prolonged stirring [24]. Similar procedures can be used for other high-polar liquids [25]. The obtained solutions are stable colloidal solutions of fullerene with dense clusters [10].

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Study of nonpolar fullerene solutions was quite detailed because solutions of this type were initially used in fullerene production [26]. The interest gradually shifted to high-polar, especially water, fullerene solutions due to applications in medicine. A challenging task of obtaining molecular fullerene-water solutions exists (initially, C_{60} is insoluble in water). Polar solutions of C_{60} (e.g., in alcohols, nitrogen-containing solvents, and others) in this respect present an intermediate system between well-studied nonpolar solutions and actual high-polar solutions in water. Cluster growth and solvatochromism in these solutions are very well pronounced and the solution can be considered a «model» system for studying chemical physics of cluster state of fullerene in liquids.

A theoretical description of kinetics of cluster growth in fullerene solutions is important from both fundamental and practical points of view. For practical tasks, understanding the evolution and dependence of cluster size distributions in C_{60} solutions on solution properties could lead to ideas for control of cluster state. From fundamental viewpoint, a kinetic theory of aggregation of fullerene molecules in solutions of different polarities would be a good step forward. While the kinetic equations are usually developed for crystal growth of micrometer size [27, 28], in our case we have clusters of maximum several hundred nanometers in size. Growth of aggregates, composed of large numbers of fullerene molecules, being a quasispherical nanoparticles of fixed size, is a peculiar process to study theoretically. The developed models could give new insights in the description of clustering processes in various systems.

In this work we present results of detailed study of cluster growth and accompanying processes in fullerene solution of N-methyl-2-pyrrolidone (NMP). This solvent is a polar liquid (dielectric permittivity, $\varepsilon = 32$), with molecule having two electronegative atoms: oxide and nitrogen. First, we review the experimental investigations and facts concerning the C_{60}/NMP system — these mainly concern the details of formation of C_{60}–NMP charge-transfer complexes, their relation to solvatochromic effect and cluster growth. Then we describe theoretical modeling of the kinetics of cluster growth and complex formation in this solution in terms of cluster-size distribution functions for fullerene. Two different models, proposed by us lately, are described and analyzed here in a new way. For each approach methods of estimation of model parameters are described. Next, we discuss the benefits of the developed approach and perspectives ahead. Finally, the conclusions are made.

2. EXPERIMENTAL STUDY OF C_{60}/NMP SOLUTION

Saturation concentration of C_{60} in NMP is approximately 0.9 mg/ml [12, 13]. Preparation of a purple colored molecular solution, denoted further as a «fresh» C_{60}/NMP solution, requires the use of mechanical stirring for a certain time (up to

30 minutes). Right after preparation, the UV-Vis spectrum of the «fresh» solution resembles that of a molecular solution in nonpolar solvent (e.g., hexane, toluene, benzene) (Fig. 1, line *1* and the inset). With passing time the characteristic «molecular» peak at 330 nm gradually disappears and the spectrum becomes a smooth exponential decay (Fig. 1, line *2*) [6, 22]. As is mentioned in Introduction, preparation can affect the kinetics of cluster or complex formation in fullerene solution. In case of C_{60}/NMP if the solution is prepared without stirring, the initial spectrum is already smeared and basically absorption only grows with time due to dissolution of microcrystals.
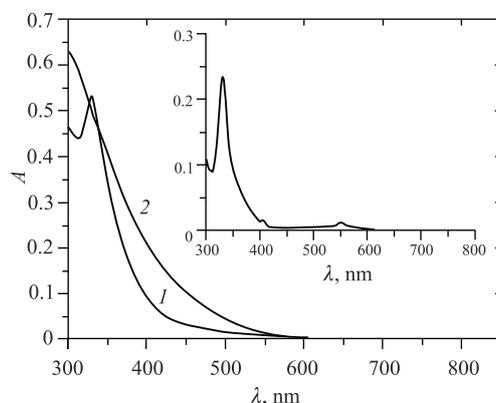
Fig. 1. Evolution of the UV-Vis spectrum of C_{60}/NMP solution. *1* — «fresh» prepared solution. *2* — solution spectra after some time has passed. Inset — typical spectrum of a molecular fullerene solution

The temporal solvatochromic effect (change of UV-Vis spectrum, Fig. 1) in C_{60}/NMP corresponds to formation of charge-transfer complexes between solved C_{60} molecules and NMP [22]. The spectrum continues to change (smear) within a few weeks, thus the formation of final C_{60}-NMP complexes is a rather slow process. It is interesting to mention, that at the initial stages of complex formation, the peak at 330 nm (and the initial «molecular» spectrum) can be almost completely restored by addition of NMP or water to the solution.

Fullerene clusters at the final stages of evolution of C_{60}/NMP solution have been analyzed by dynamic light scattering (DLS) and visualized by transmission electron microscopy (TEM). The cluster size distribution is broadly polydisperse, thus DLS gives an approximate value of the mean cluster size. The values of the aggregate sizes obtained from DLS are of the order of 500 nm. This result is supported by the TEM image of dried solution (Fig. 2). The polydispersity of aggregates is also confirmed by TEM. Additionally, small-angle neutron scattering (SANS) experiments show, that in C_{60}/NMP cluster sizes are above 100 nm.
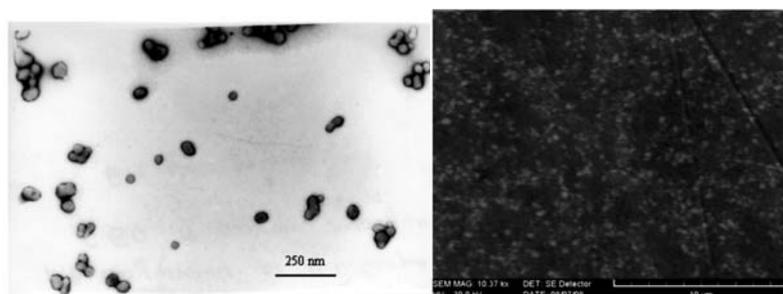
Fig. 2. Transmission electron microscopy image of C_{60}/NMP solution

In work [9] SANS was used to study the ternary system C_{60}/NMP/water. It has been shown, that the pure C_{60}/NMP solution reveals no SANS signal in the measured range of q-values. This means, that cluster sizes are beyond the range of 1–100 nm, which is the particle size resolution of SANS.

While certain knowledge about final cluster state exists, the data on the kinetics of cluster growth, and the size distribution in the «fresh» solution and during the evolution of the system are poor. From the UV-Vis spectrum of «fresh» solution, we can suppose that it is molecular. The following evolution of UV-Vis spectrum reflects the kinetics of complex formation and does not reveal information about cluster growth. Yet, utilizing the extraction experiment one can obtain as the additional information the evolution of free (monomer) C_{60} concentration [11]. This is done by fullerene extraction into hexane by a procedure described in [11] (see Fig. 3). Performing extraction at different time
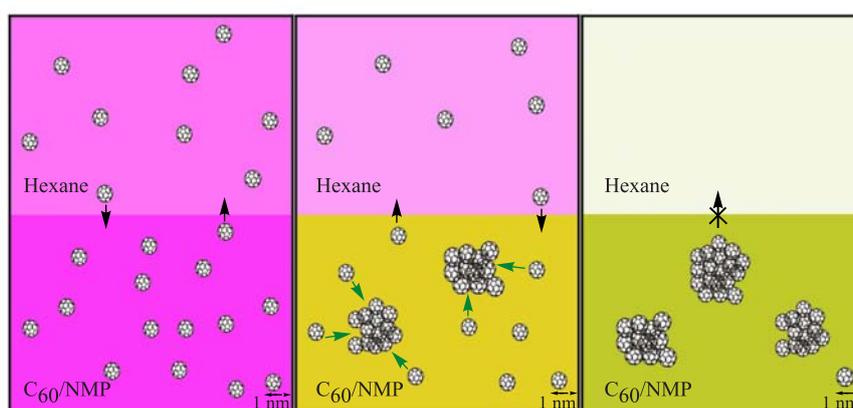
Fig. 3. Representation of extraction of fullerene into molecular solution in hexane from C_{60}/NMP at different stages of the evolution of solution

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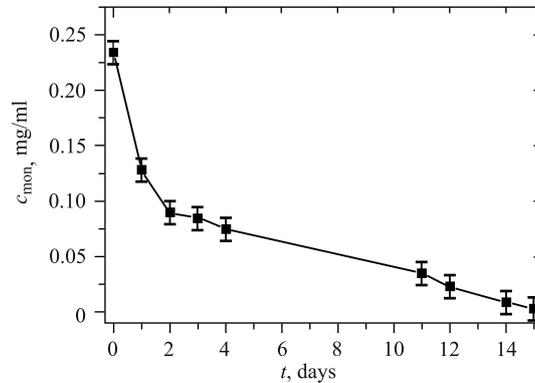
Fig. 4. Evolution of C_{60} monomer concentration in C_{60}/NMP

stages, the evolution of monomer concentration in C_{60}/NMP has been obtained (Fig. 4). At the final stages of cluster growth no fullerene is extracted into hexane (C_{60} concentration in hexane is zero, within experimental resolution, as revealed by UV-Vis). This result indicates that all of the concentration C_{60} is in form of aggregates.

To summarize, in C_{60}/NMP solutions at room temperatures at any concentration fullerenes form charge-transfer complexes with solvent molecules. The process of complex formation quickly influences the UV-Vis spectrum of solution in a qualitative way and continues for about a month. Complex formation is connected (probably, being one of the reasons) with the slow growth of large dense and stable fullerene clusters in C_{60}/NMP with sizes up to 500 nm.

3. BASIC KINETIC EQUATIONS FOR CLUSTER GROWTH IN C_{60} SOLUTIONS

For the aim of theoretical description of kinetics of cluster growth in C_{60}/NMP solutions we utilize the approach formerly developed for description of nucleation processes and corresponding particle segregation during phase transitions [19, 29–32]. In this approach, the time evolution of cluster size distribution function $f(n, t)$ is obtained from a set of ordinary differential kinetic equations. The main assumptions made in order to obtain the equations are that clusters are quasispherical particles with densities that of a macroscopic solid phase and that cluster growth or decomposition occurs only via attachment and detachment of a single particle (a monomer) to the cluster. Second assumption works well for initial stages of cluster formation and growth and could be reconsidered for later stages. Yet, we shall stay within this approach for the sake of simplicity of results, thus obtaining a qualitative picture and some general estimation. The

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formulated model takes the form of a very simple system of kinetic equations:

$$\frac{\partial f(n,t)}{\partial t} = w_{n-1,n}^{(+)}f(n-1,t) + w_{n+1,n}^{(-)}f(n+1,t) - w_{n,n+1}^{(+)}f(n,t) - w_{n,n-1}^{(-)}f(n,t),$$

(1)

where $w_{n,m}^{(\pm)}$ is the probability of a cluster to attach / detach a monomer and change its size from n to m per time unit (m being $n+1$ or $n-1$). Here and later in the text, «cluster of size n» is a cluster, composed of n monomers. Equations (1), with the addition of boundary conditions and introduction of certain modifications will be a basis of calculations of $f(n,t)$ evolution.

From a thermodynamic consideration, the ratio between probabilities of monomer attachment and decomposition from a cluster depends on the work of cluster formation, $\Delta G(n)$ [29, 33]:

$$\frac{w_{n-1,n}^{(+)}}{w_{n,n-1}^{(-)}} = \exp\left\{-\frac{\Delta G(n) - \Delta G(n-1)}{k_B T}\right\},$$

(2)

where $\Delta G(n)$ is the change in Gibbs free energy of the solution if n monomers form a cluster. Thus, if a certain expression for w^+ and $\Delta G(n)$ is given, equations (1) are completely settled.

The expression for probability of monomer attachment is obtained from a consideration of diffusion of monomers from bulk solution to the surface of the cluster of size n [29, 30]:

$$w_{n,n+1}^{(+)} = 4\pi Dc\left(\frac{3v_s}{4\pi}\right)^{1/3} n^{1/3},$$

(3)

where D is the diffusion coefficient of monomer in solution, c is their concentration and v_s is the volume per particle in cluster.

For work of cluster formation, $\Delta G(n)$, it was shown in the previous works [19, 34], that the classical liquid drop model is inapplicable for description of cluster growth in fullerene solutions. A modification into expression for $\Delta G(n)$ leads to the so-called limited growth model [29]:

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

(4)

In Eq. (4) the first two terms correspond to the liquid drop model and represent the volume and surface terms, respectively. With the third term, as in Eq. (4), and $k > 0$, $\beta > 1$ the cluster growth is limited (clusters are stabilized) at a certain size [34]. The expression for difference of monomer chemical potentials in bulk solution and in cluster, $\Delta\mu$, is taken as for an ideal solution:

$$\Delta\mu = k_B T \ln\left(\frac{c_0}{c_{\text{eq}}}\right),$$

(5)

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where c_0 is the time-dependent concentration of monomers of the segregating phase (single-fullerene molecules) and c_{eq} is the equilibrium concentration with respect to aggregation. If solution concentration, c, is above c_{eq} (supersaturated solution) then cluster growth takes place. If c is below c_{eq} (unsaturated solution) then the molecular solution is stable. It should be mentioned here, that c_{eq} is the equilibrium concentration with respect to cluster growth and thus it can be unequal and even many times different from the solution saturation concentration, c_{sat}.

4. DESCRIPTION OF CLUSTER GROWTH IN C$_{60}$/NMP SOLUTION

4.1. General Remarks. If for nonpolar C$_{60}$ solutions (e.g., in benzene, carbon disulfide), Eqs. (1)–(4) can be used as a qualitative model of the observed cluster growth after nonequilibrium preparation [19, 35], they are not applicable for description of observed cluster state in polar fullerene solutions, like C$_{60}$/NMP. A number of discrepancies between theoretical results and experimental facts exist. Namely, the cluster size distributions, obtained in limited growth model are too narrow compared to experimental results [36]. Another reason to search for alternative models is that using Eq. (4) we obtain stabilization by a certain value of cluster size n [34], while more realistic would be to obtain confinement of growth by time, t. Another requirement is taking account of the formation of charge-transfer complexes and their evident connection with cluster formation and growth processes. These models are the object of present paper and will be described, discussed and compared next.

Two models of cluster growth in C$_{60}$/NMP were proposed lately [37, 38] and are formulated and further developed here. In both models the equilibrium concentration for cluster growth is much less than saturation concentration $c_{eq} \ll c_{sat}$. In the first model c_{eq} is attributed to concentration of free fullerene molecules in C$_{60}$/NMP and the process of formation of charge-transfer complexes is considered to directly confine cluster growth. In the second model, a more complex approach is used: the free C$_{60}$ in NMP are unsaturated and do not aggregate up to c_{sat}. The cluster growth is a consequence of complex formation: free fullerenes tend to form charge-transfer complexes with NMP and the solution of these complexes is highly supersaturated. The cluster growth is limited similarly as in the first model by final complex formation.

General analysis and comparison of results of solution of the kinetic equations (1) is based on the obtained evolution of cluster size distribution function $f(n, t)$. The integral properties of cluster state that will be analyzed are the mean cluster size in solution and concentration:

$$\langle n \rangle = \frac{\sum\limits_{n=1}^{N} n f(n, t)}{\sum\limits_{n=1}^{N} f(n, t)}, \quad c(t) = \sum\limits_{n=1}^{N} n f(n, t). \tag{6}$$

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In sums over cluster sizes in (6) and later in the text, N, corresponds to the maximum cluster size n that is present in the solution at a given time t. $c(t)$ is the total concentration of segregating particles in the solution. Various integration ranges can be taken in (6) to obtain mean cluster sizes and concentrations of certain fractions in the solution.

4.2. Model of Confined Cluster Growth in C_{60}/NMP Solution. A basic straightforward approach would be to suppose from the experimental data (cluster growth observed in C_{60}/NMP at any concentration) that the solution of C_{60} is highly supersaturated with respect to cluster growth, and the effect of complex formation on aggregation is its eventual confinement [37]. One new model parameter — characteristic time of C_{60}-NMP complex formation, τ, to reflect the influence of growth confinement into probabilities of monomer attachment / detachment is introduced:

$$w_{m,n}^{(\pm)}(t) = w_{m,n}^{(\pm)} e^{-t/\tau}. \tag{7}$$

In (7), the probabilities of growth and shrinking on the right-hand side of equation are defined by (3) and (2), and in fact are also time-dependent via monomer concentration. Introducing (7) into (1), we obtain that the right-hand side of kinetic equations decreases exponentially with time — cluster growth (and shrinking) is
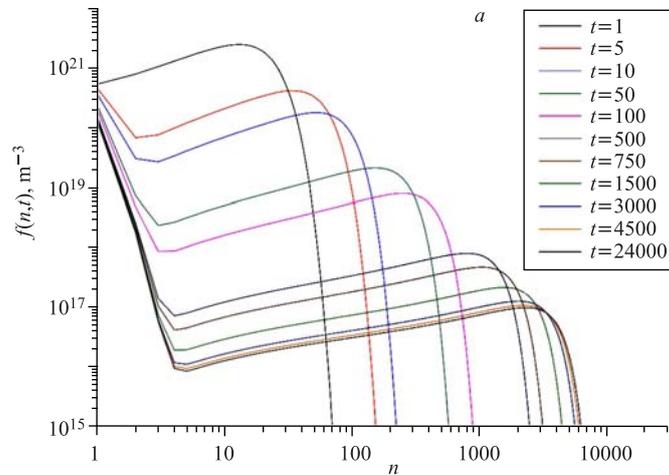
Fig. 5. Modeling results of evolution of cluster state in C_{60}/NMP solution in the framework of confined growth model. *a*) Evolution of cluster size distribution function, $f(n,t)$; *b, c*) evolution of the average cluster size: $\langle R \rangle$ (*b*), and monomer concentration, c_{mon} (*c*) for different values of model parameter τ. Calculation parameters: $c_0/c_{\mathrm{eq}} = 10^4$, $\alpha_2/k_B T = 8$, $c_0 = 8.3 \cdot 10^{23}$ m^{-3}

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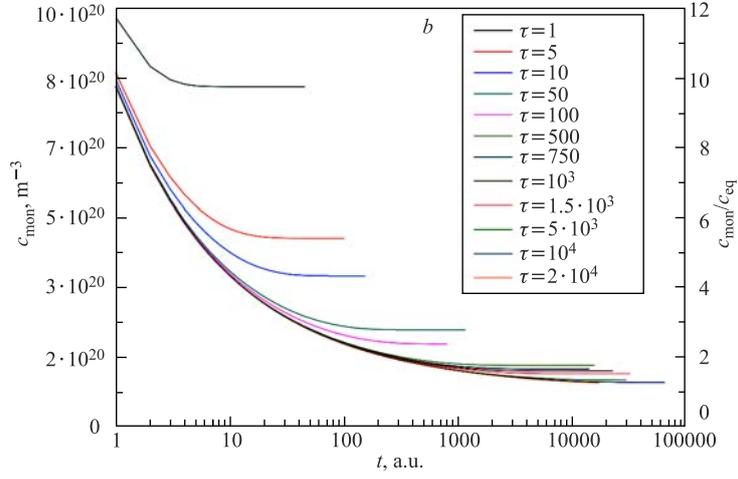
Fig. 5, b
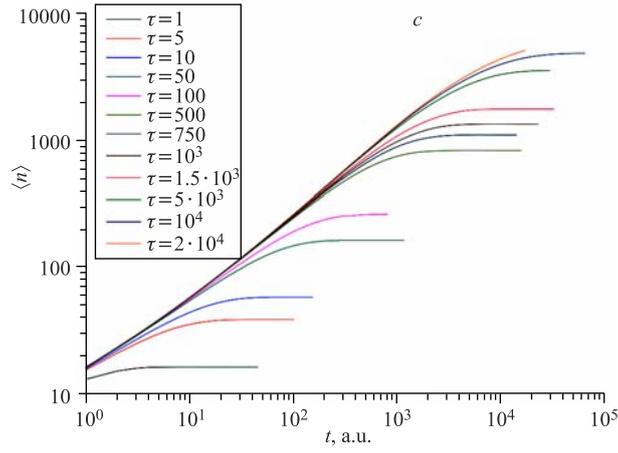
Fig. 5, c

eventually confined. The initial and boundary conditions for $f(n, t)$ will be used in the common form:

$$f(1, 0) = c_0,$$
$$f(n, 0) = 0, \quad n > 1, \qquad (8)$$
$$\sum_{n=1}^{N} n f(n, t) = c_0 = \text{const},$$

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which means, that fullerene concentration, c_0, is constant at any moment of time, and the initial solution state is c_0 monomers with no clusters. The value for c_{eq} can be roughly estimated from Fig. 4 as no more than 10^{-3} mg/ml.

The results of the described model are presented in Fig. 5. Basing on experimental evidence, we consider here only considerably large values of τ so that complex formation influences only the latest stages of cluster growth. Cluster size distribution function is broad at large cluster sizes, in qualitative agreement with experiment (Fig. 5, a). The time evolution of average cluster size, $\langle n \rangle$ (or $\langle R \rangle$ in terms of cluster radius in nanometers), for different values of model parameter τ (Fig. 5, b) is similar, expected growing of limited value of $\langle R \rangle$ is observed. The found limits of $\langle R \rangle$ in Fig. 5, b are far from the real value, which means that significantly larger τ values should be used in order to attain agreement with experimental data. The value of τ can be estimated from the $\langle n \rangle$ vs. τ dependence obtained at smaller cluster sizes considered in this work (Fig. 6, a). It is fitted by the power-law dependence:

$$\langle n \rangle = a\tau^b, \quad a = 17.6 \pm 1.5, \quad b = 0.60 \pm 0.01. \tag{9}$$

As can be seen from Fig. 6, a, the fitting is not an exact approximation for real dependence, partly because the $\langle n \rangle$ values obtained for a given τ value (from Fig. 5, c) are only estimates of extrapolation. Another reason may be a deviation from dependence given by (9) at larger values of τ, which reflects the real dependence of mean cluster size for liquid drop model [19, 34]. The precise analysis and calculations are under way. Using Eq. (9), a qualitative estimate of values of relaxation time τ, and $\langle n \rangle \sim 10^7$ (corresponding to $\langle R \rangle \sim 100$ nm) is $\tau \sim 10^9$. It should be mentioned, that the dependence of Fig. 6, a is strongly influenced by the value of initial supersaturation $c_{mon}(0)/c_{eq}$ which at present cannot be obtained directly from experiment.

Comparing monomer concentration evolution from model (Fig. 5, c) with experiments on fullerene extraction into hexane (Fig. 4), we see that theoretical concentration drops too fast with time. As a possible explanation of this difference, one can take into account that not only monomers of C_{60} but small nonstable clusters may be extracted into hexane. These clusters can easily break into single fullerene molecules at the interface and pass it. Thus, these clusters must be also taken into account in the equation of balance between C_{60}/hexane and C_{60}/NMP system. In Fig. 6, b the evolution of concentration of monomers and small C_{60} clusters is presented for different values of N in (6). For values of $N \leqslant 10$ the $c_N(t)$ agreement with experimental data is still not reached — concentration drops from c_0 to c_{eq} within 10^3 a.u. (less than one second). For $N = 10^2, 10^3, 10^4$ the decreasing lines are almost parallel to each other and take approximately two–three orders of t. These results can be treated as qualitatively corresponding to experimental dependence in Fig. 4. Yet, the values of N are

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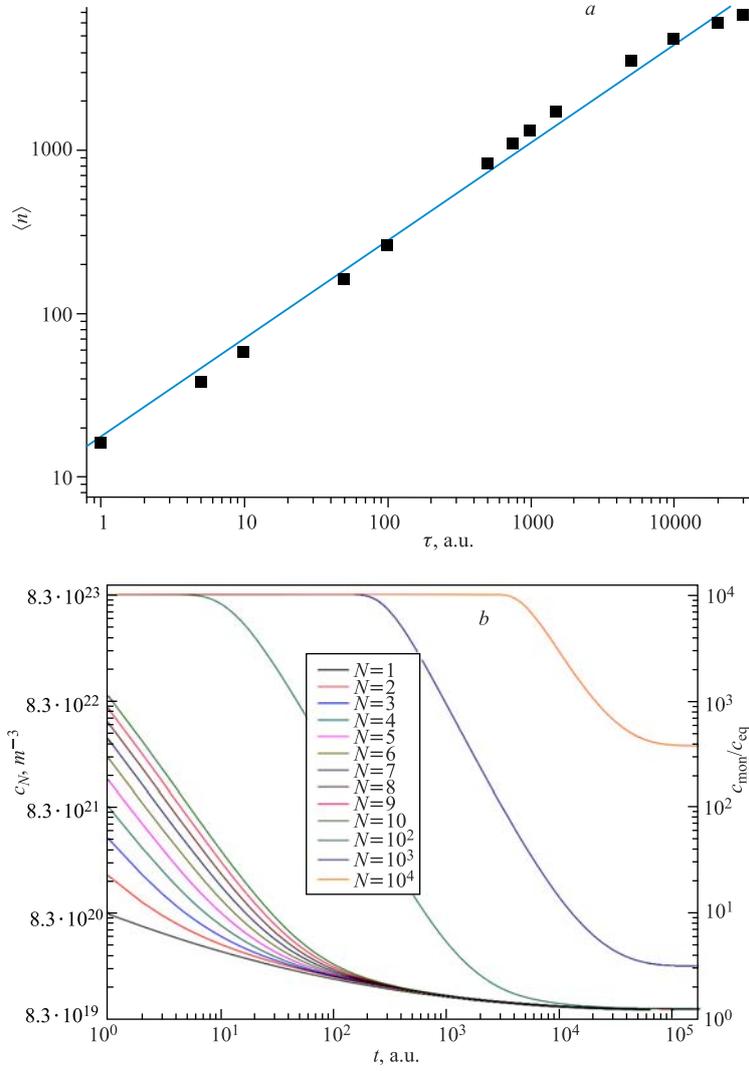
Fig. 6. *a*) Dependence of the final mean cluster size $\langle n \rangle$ in solution on model parameter τ. *b*) Evolution of monomer, monomers with small clusters concentration with time. Dependence on limits of sums, N, for $\tau = 2 \cdot 10^4$. Calculation parameters: $c_0/c_{eq} = 10^4$, $\alpha_2/k_B T = 8$, $c_0 = 8.3 \cdot 10^{23}$ m^{-3}

quite large to suppose, that clusters of this size are so weak, that they break at the liquid interface to pass to hexane. Thus, the $c_{mon}(t)$ dependence (Fig. 5, *c*) is a weakness of the proposed model. Moreover, while the presented model can be

applied for description of kinetics of cluster growth in C_{60}/NMP solutions, it is not so clear, why the solution of free C_{60} molecules is highly supersaturated in NMP. In the frame of nonpolar solutions, it would be meaningful to propose a model where free fullerenes do not tend to form clusters in polar solvents also, thus keeping this notion general for any solvent. This model is presented next.

4.3. Two-Step Cluster Growth Model for C_{60}/NMP Solution. In opposite to Subsec. 4.2, we can suppose that free C_{60} molecules in NMP (a polar solvent), as also is the case of nonpolar solvents, do not form clusters up to saturation concentration c_{sat}. Thus, cluster formation should be a consequence of a certain influence. In the case of nonpolar solutions it is nonequilibrium preparation [18–20]. For polar solvents, we can suppose that the reason for aggregation is the formation of charge-transfer complexes between fullerene and solvent molecules. As soon as they are formed in the solution, the charge-transfer complexes C_{60}-NMP start to form clusters [38]. Thus fullerene aggregation is considered as a two-step process. With respect to cluster growth, free fullerene molecules solution is unsaturated, but with respect to complex formation it is unstable even at very low concentrations. The growth of aggregates from C_{60}-NMP complexes must still be confined in a certain way. We choose here again Eq. (7) to describe confinement, the reason for it being either the final formation of complexes and short-order structure around clusters, or some other interaction. The modified system of kinetic equations for this model is the following:

$$
\begin{cases}
\dfrac{dA(t)}{dt} = -\dfrac{A(t)}{\tau_c}, \\[2mm]
\dfrac{\partial f(1,t)}{\partial t} = w_{2,1}^-(t)f(2,t) - w_{1,2}^+(t)f(1,t) + kA(t), \\[2mm]
\dfrac{\partial f(n,t)}{\partial t} = w_{n-1,n}^+(t)f(n-1,t) + w_{n+1,n}^-(t)f(n+1,t) - \\[2mm]
w_{n,n+1}^+(t)f(n,t) - w_{n,n-1}^-(t)f(n,t), \quad n > 1, \\[2mm]
f(n,0) = 0, \quad \forall n, \\[2mm]
A(0) = c_0 = \text{const.}
\end{cases}
\tag{10}
$$

Here, $A(t)$ is the concentration of free C_{60} molecules in the solution, τ_c is the parameter reflecting the characteristic time of C_{60}-NMP complex formation. As in the previous section the initial state here is also the molecular solution C_{60}/NMP of concentration c_0.

The evolution of $f(n,t)$ and cluster state parameters depend generally on the relation of model parameters and initial conditions — τ_c, τ, c_{eq}, c_0. When τ_c is sufficiently small (fast complex formation) model gives the same results as confined growth. Indeed, in this case major part of free fullerene concentration

forms complexes with NMP quickly and the two steps of cluster growth proceed independently (different time scales of complex formation and cluster growth). Contrary to that, when τ_c is sufficiently large (slow formation of complexes) and c_{eq} is also much less than c_0, cluster growth at conditions of monomer input into solution takes place for a certain amount of time. This indeed is the case of fullerene solutions and it will be discussed here. It must be mentioned, that comparison of temporal parameters (τ_c, τ) is done in respect to rate of cluster growth, which is fast for C_{60} solutions and is determined by fullerene and solution parameters [19]. Certain additional details on regimes of cluster growth in this model are discussed in [38].

The results of calculations in frame of the model, e.g., evolution of cluster size distribution function $f(n,t)$, monomer concentration and cluster size on t, are presented in Fig. 7. The value of τ in calculations is $1.5 \cdot 10^3$, equal to one of the values in the previous section. A direct estimation of τ_c from experimental data (Fig. 4) can be made by fitting with classical exponential decay from initial value of c_0: $A(t) = c_0 e^{-t/\tau_c}$, which gives the rough value of $\tau_c \sim 70$ h, or $\tau_c \sim 10^{10}$ a.u. With an estimate of τ from section above, the choice of τ_c around the value of 10^2 for model calculations seems reasonable (τ_c is of the same order, or somewhat less than τ).

The evolution of cluster size distribution function with time is presented in Fig. 7, a. The formed large clusters peak is well-pronounced and not as broad
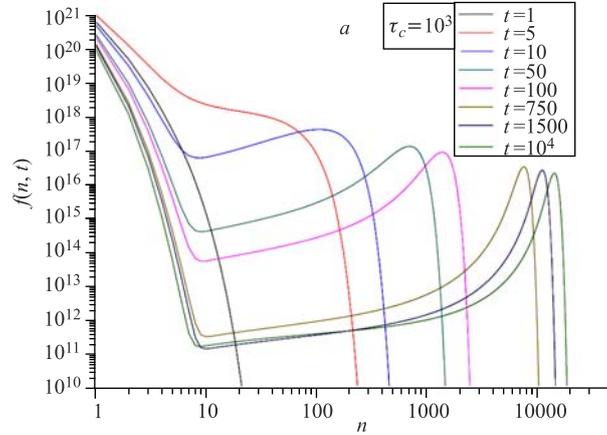
Fig. 7. Modeling results of evolution of cluster state in C_{60}/NMP solution in the framework of two-step growth model. a) Evolution of cluster size distribution function, $f(n,t)$; b, c) evolution of the average cluster size, $\langle R \rangle$ (b), and monomer concentration, c_{mon} (c) for different values of model parameters. Calculation parameters: $c_0/c_{eq} = 10^4$, $\alpha_2/k_B T = 8$, $c_0 = 8.3 \cdot 10^{23}$ m^{-3}, $\tau = 1.5 \cdot 10^3$

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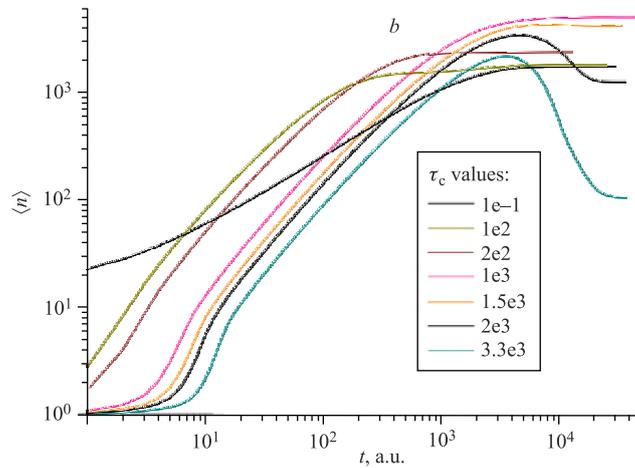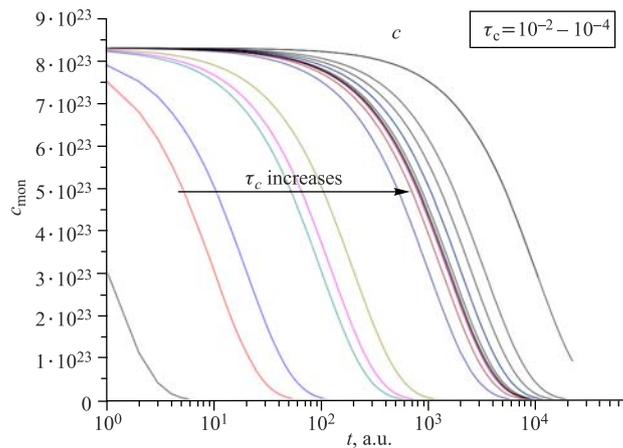
Fig. 7, *b*

Fig. 7, *c*

as in the previous model. Evolutions of monomer concentration and mean cluster size with time are presented in Fig. 7, *b* and *c*, respectively. In the framework of the present model with two relaxation times, qualitatively different regimes of system evolution may be observed, depending on the ratio of τ_c and τ for other parameters fixed. As was already mentioned above, two limiting cases correspond to situations, when the relations $\tau_c \gg \tau$ or $\tau_c \ll \tau$ hold. In case when complex formation (τ_c) is much slower than cluster growth confinement (τ) a considerable

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amount of monomer C_{60}-NMP complexes will be present in the final state of solution. This result would contradict experimental facts [11]. Thus, τ_c should be of the order of τ or lower. As can be seen from Fig. 7, b at $\tau_c \sim \tau$ a change of regime from monotonic growth of mean cluster size with time (up to a certain value) to nonmonotonous behavior takes place. With further increase of τ_c a maximum is revealed.

The presented in this section model is suitable for qualitative description of kinetics of cluster growth in C_{60}/NMP solution. An estimate of model parameters for selected values of supersaturation ($c_0/c_{\mathrm{eq}} = 10^4$) has been performed. The work on obtaining solutions for these large values of τ_c, τ and t is under way.

5. DISCUSSION

The description of cluster growth by differential kinetic equations provides one with the possibility to obtain cluster size distribution functions for the system at any time moment. Incorporation of additional knowledge of system properties and effects affects qualitatively the time dependences of mean aggregate size and other cluster state (and the system, generally) properties. In the present work, the type of population-balance equations were used for modeling of C_{60}/NMP solution kinetics. Both proposed in the presented work models suppose that the charge-transfer complex formation in C_{60}/NMP has a general impact on cluster growth processes in the solution. This is in agreement with experiments [6, 11, 39], from which is also seen, that both these processes have the same order of values of relaxation times. At least, none of the processes is negligibly fast (or slow) compared to others. Together with evident interference of these processes, it is clear that they must be always accounted in theoretical models or treatment of experimental facts. In this work we provide a possibility for further understanding in this field.

Two interesting problems, connected with aggregation and irreversible processes in general were partly addressed in the work: What is the initial reason for the cluster growth to start and what is the further reason for it to stop? Aggregation takes place when the concentration of segregated particles exceeds a certain limiting (or critical) value, making the solution supersaturated. Basic cluster growth models consider clusters as small volumes of solid phase in the solution. While it cannot be the case for other certain systems, it seems to be quite true for fullerene solutions basing on experimental evidence [10, 20]. In this case, the saturation concentration with respect to cluster growth should be equal to saturation concentration of solution of fullerenes. Yet, if the clusters are still observed in the solution, then there must be a certain supersaturation in respect to aggregation. It can be nonequilibrium preparation or change of the state of particles already in solution. The second supposition is complex: new state of

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particles should be energetically favorable with respect to initially dissolved state and also must be supersaturated with respect to cluster growth. Further, one must answer the question: Why particles do not dissolve directly into the «new state» form? This process of dissolution either may be not allowed or the time of formation of the new state could be much longer than dissolution — that is, the initial dissolved form could be kinetically favorable. Once the aggregation has started, it would generally stop only when all the excess concentration of particles is in the form of clusters. The mechanism of Ostwald ripening states that the more thermodynamically energetically favorable state is larger clusters in respect to small clusters [40–43]. The system thus tends to a state with one or several huge clusters in equilibrium with a saturation concentration of monomers. While in experiment a different situation is observed a certain stabilization mechanism must be introduced to explain the cluster state. The composition of relation of probability of cluster growth to cluster shrinking (Eq. (2)) in case of liquid drop model is so that kinetic stabilization, when a certain cluster size distribution is stable because w^+ and w^- are equal, is not realized. Among some regularly met effects responsible for stabilization are specific cluster structure, which makes a certain cluster size energetically favorable [44, 45] and a general mechanism of stabilization via charged surfaces of colloids [46, 47]. In our case, we utilize the limited growth model for nonpolar solutions (Eq. (4)), and confinement of cluster growth due to complex formation (Eq. (7)).

The first confined growth model provides a simple and general description of a continuous attenuation of cluster growth in a solution with a single additional model parameter τ. Thus, it can be expected to be qualitatively appropriate for many systems, where aggregation slowly stops with time, providing a broad cluster size distribution. The second model introduces two parameters and a two-step aggregation process. An interesting outcome of the model formulation is the fact, that complex formation should be an indicator of cluster growth in fullerene solution. Therefore, if complex formation initiates cluster growth, then the observation of a temporal solvatochromism for a given fullerene solution can be used to implicitly predict cluster formation and growth. Moreover, using modeled evolution of different fractions concentrations in the solution it could be possible to predict the cluster size dependence on evolution of the UV-Vis spectrum.

Another point to be discussed is the initial conditions used in the modeling. A monomer solution is a convenient initial state for theoretical modeling and was used in this work for the calculations to present qualitative behavior of cluster state. A regular preparation of C_{60} in NMP implies stirring for several hours. This is done partly because without stirring dissolution of fullerene proceeds slowly and also because with «correct» stirring a more «molecular» C_{60}/NMP solution is obtained. If C_{60} is dissolved without stirring, preliminary experiments show that most of the concentrations form charge-transfer complexes before dissolution

ends. Thus, the time of dissolution is of the same scale as are the characteristic times of complex formation, and, presumably, cluster growth confinement. Therefore, the kinetics of dissolution (with or without stirring) should be incorporated in the kinetic equations for better comparison with experiment. To do this, a number of experiments to study kinetics of fullerene dissolution should be made and interpreted. Indeed, it would also be interesting to study the kinetics of C_{60} dissolution in nonpolar solvents, where the UV-Vis spectroscopy gives an easy way to measure the evolution of concentration [48].

Valuable information in general and for the developed theory could be given by microscopic simulation of formation and equilibrium properties of C_{60}-NMP complex. Similar modeling has been performed for C_{60} complexes with different molecules using the density functional theory (DFT), molecular mechanics, molecular dynamics, etc. [49–53]. The computer simulation can be used to predict the optimal number of NMP molecules around C_{60} and their equilibrium configuration, the thermodynamic properties of formation of the complex. These data can be incorporated into the kinetic equations via characteristic time of complex formation. From the analysis of the properties of C_{60} with one and several NMP molecules both times for two-step growth model, τ_c and τ, could be estimated. The future development of the proposed theoretical approach will also be the estimation and incorporation of cluster–cluster aggregation effects in kinetic equations. In parallel, using the roughly estimated model parameters in this work we plan to obtain the cluster size distribution functions for C_{60}/NMP within model framework and qualitatively model evolution of the UV-Vis spectra.

CONCLUSIONS

In the present paper the kinetics of cluster growth in fullerene C_{60} solution in a polar solvent NMP were considered. A review of experimental study is presented. Two theoretical models to describe the time evolution of cluster size distribution function are proposed. These models take into account the formation of C_{60}-NMP charge transfer complex as an impact on cluster state evolution. In the first model, complex formation is considered to be the reason for confinement of cluster growth in the initially supersaturated fullerene solution. In the second model, cluster growth is considered to be a two-step process, with complex formation itself being the reason for the start of cluster growth. For both models, the evolution of cluster size distribution function $f(n, t)$ and cluster state properties, average cluster size $\langle R \rangle$ and concentration of fractions were obtained for a set of model parameters. Using these results and general considerations on structure of kinetic equations (1), (7)–(9), the values of model parameters for agreement with experiment were obtained. Both models can be used for further description of experiments, yet for model of confined growth the dependence

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of C_{60} monomer concentration, c_{mon}, decreases too sharp in comparison with measurements. The directions of the further research were discussed.

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