The kinetics of dissolution and cluster formation of fullerene in polar and low polar solutions

N. Jargalan[1,*], D. Sangaa[1], T.V. Tropin[2], M.V. Avdeev[2], V. L. Aksenov[2, 3]

[1]*Institute of Physics and Technology, Mongolian Academy Sciences, Ulaanbaatar, 13330, Mongolia*

[2]*Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, 141980, Dubna, Russia*

[3]*National Research Centre "Kurchatov Institute", 123182, Dubna, Russia*

Fullerene and fullerene like nanostructures play a main role in various research areas. The amount of investigations of fullerene C_{60} and C_{70} has grown up considerably due to their several unique properties [1-2, 6]. In this report we present theoretical models for cluster growth, the modeling of small angle neutron scattering curves, and the results of structural analysis (SANS) for polar solutions of these macromolecules. Investigation of kinetics of dissolution and complex formation are studied for C_{60}/Benzene, C_{60}/Toluene and C_{60}/N-methyl-2-pyrrolidone (NMP) solutions of various concentrations by UV-Vis spectrometry. We model the kinetics of simultaneously occurring processes in the solution via a system of basic kinetic equations and obtain the corresponding parameters dependence on preparation conditions. The investigation of structural properties of fullerene C_{70} solution in CS_2 was performed at the YuMO instrument of the IBR-2 reactor. The results are compared to molecular dynamics simulations, and other research works.

Key words: Fullerene, cluster growth, dissolution, complex formation, solution, small angle neutron scattering, UV-Vis,

1. INTRODUCTION

Nowadays, the properties of fullerene in solvents have attracted much attention because of their perspective biomedical applications. Fullerenes dissolve well in various solutions in different amounts, which depend on solvent polarity. In general, fullerenes dissolve well in organic and low polar solvents, dissolve weakly in polar solvents, and do not dissolve in high polar liquids [1]. In polar solvents (e.g. NMP, Pyridine), fullerene show a few interesting properties such as cluster formation, solvatochromic effects due to change of polarity or formation of complexes between fullerene and solvent molecules [2], non-liner dissolution properties [3] etc.

Investigation of kinetic processes, especially cluster growth and dissolution, are important from both fundamental and practical viewpoints. On one hand, understanding the evolution of cluster size distributions, depending on dissolution conditions of the solutions could allow controlling of the cluster state. On the other hand, a kinetic theory of aggregation is extended to a wide range of sizes (several hundred nanometers).

2. INVESTIGATION OF CLUSTER FORMATION IN DIFFERENT SOLUTIONS

Experimental study of cluster formation in various solvents by small angle neutron scattering

Small-angle neutron scattering (SANS) is an especially useful technique for investigations of structural properties in fullerene solutions.

The cluster formation of fullerenes in C_{60}/NMP and C_{70}/CS_2 solutions was studied by SANS. C_{60}/NMP solutions were prepared at equilibrium conditions (a day before measurements) and via ultra-sonication. In this case, we were interested to compare cluster formation dependence on the age of solutions and preparation methods.

The clusters sizes obtained were above 100 nm for both solutions and did not vary for sonicated and dissolved solutions. For SANS, carbon disulfide (CS_2) is one of the most convenient fullerene solvents. A number of SANS experiments on C_{60}/CS_2 system was reported earlier [4-6] and demonstrated the value of radius of gyration R_g to be 10% higher than the calculated for a single fullerene molecule. In this case, the hypothesis of cluster or complex formation of fullerene C_{70} in carbon disulfide (CS_2) solvent was investigated by small angle neutron scattering.

Several series of samples, prepared at different concentrations of solution, as well as preparation conditions, were measured at the YuMO instrument of the IBR-2 reactor. The value of the gyration

* Electronic address: njagaa@gmail.com

radius (R_g) was evaluated from SANS to be in the range of 3.32-5.56 Å, depending on sample preparation procedure. In general, the obtained R_g values are considered to be in close agreement with theoretical estimates [4].

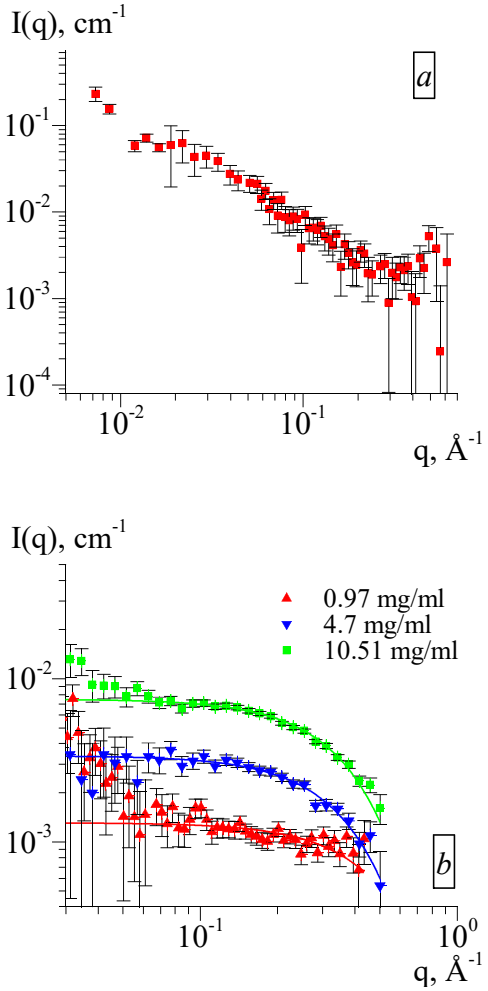

Figure 1. SANS intensity distributions for: a – C_{60}/NMP, b – C_{70}/CS_2 solutions.

A theoretical description of kinetics of cluster growth in C_{60}/NMP solution

In previous work [7] two theoretical models, namely two-step and confined cluster growth, were proposed and evaluated for C_{60}/NMP solution and polar fullerene solutions in general. In the present work we substitute in these equations the kinetic coefficients of dissolution and complex formation. Kinetic equations for the studied system are the following:

$$\begin{cases} \dfrac{dA(t)}{dt} = k\left(c_{sat} - A(t)\right) - k'A(t) \\ \dfrac{\partial f(1,t)}{\partial t} = w_{2,1}^{-} f(2,t) - w_{1,2}^{+} f(1,t) + k'A(t) \\ \dfrac{\partial f(n,t)}{\partial t} = w_{n-1,n}^{+} f(n-1,t) + w_{n+1,n}^{-} f(n+1,t) - \\ \qquad -w_{n,n+1}^{+} f(n,t) + w_{n,n-1}^{-} f(n,t) \\ f(n,0) = 0, \forall n \\ \sum_{n=1}^{\infty} n f(n,t) = c(t) \end{cases} \quad (1)$$

where, $f(n,t)$ is the cluster size distribution function, $w_{n,m}^{(\pm)}$ is the probability of a cluster to attach/detach a monomer, $A(t)$ is concentration of free monomers, k_1, k_2 are the kinetic coefficients of dissolution and complex formation respectively, $c(t)$ is the total concentration of segregating particles in solution.

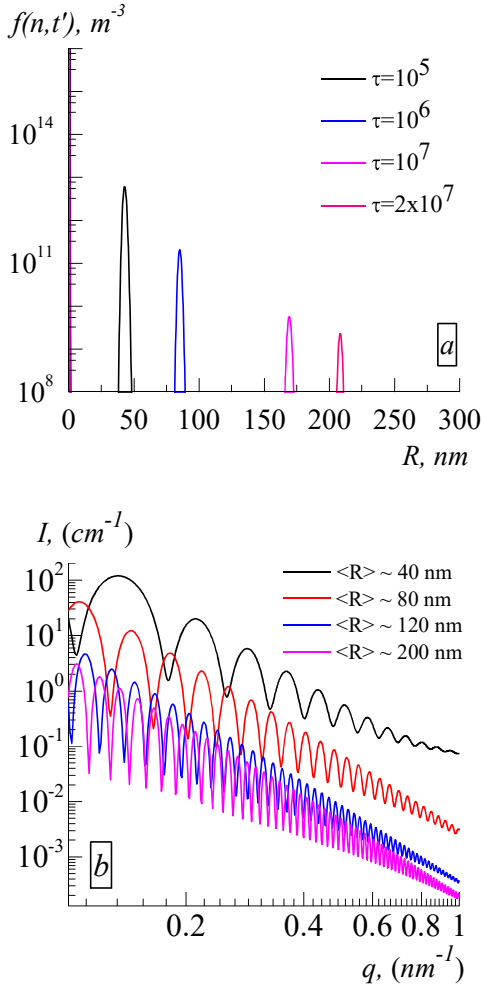

Figure 2. Theoretical calculations of cluster growth in polar fullerene solution: a – cluster size distribution functions with particle size, b – modeled SANS curves.

As the result using extrapolation methods we have obtained cluster-size distribution functions with particle sizes. Furthermore, the obtained distribution

functions are used for modeling small angle neutron scattering curves. The modeled SANS curves are presented for the systems with average cluster size of 40, 80, 120, and 200 nm (Fig. 2b). For further precise modeling of the real systems, e.g. C_{60}/NMP solution, one needs to know the values of kinetic coefficients, substituted in equations (1). Accordingly, our next investigations focused on detailed studies of dissolution and complex formation for C_{60}/NMP solution.

3. INVESTIGATIONS OF KINETICS OF DISSOLUTION OF FULLERENE IN SOLUTIONS

In this section, we investigated the kinetics of the dissolution and complex formation for solutions with different polarity using UV-Vis spectrometry method.

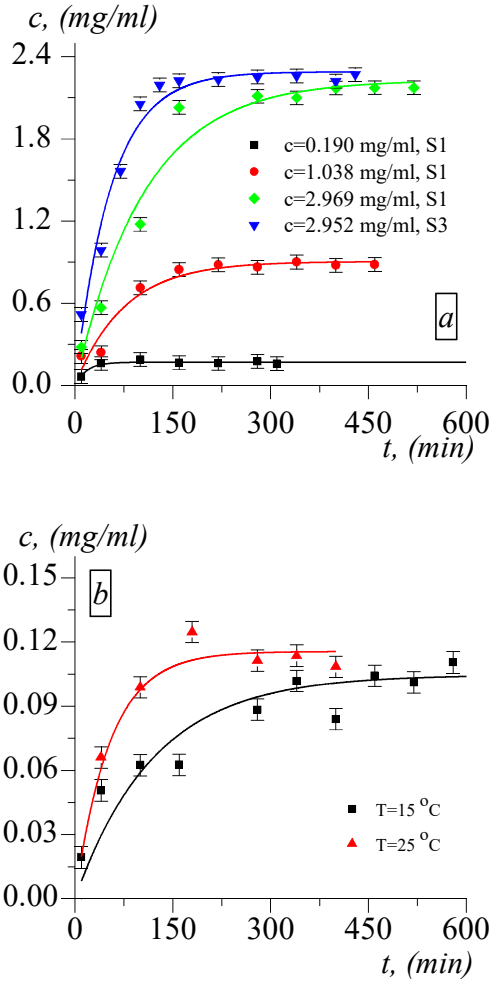

Figure 3. The evolution of concentration a – $C_{60}/C_6H_5CH_3$ solution with different stirring rates; b – C_{60}/C_6H_6 solutions at equilibrium condition and different temperatures. The symbols in the figures correspond to the experimental measurements; the curves are the approximation of the data by the equation of Noyes and Whitney.

At first, the study of C_{60} dissolution in low polar solutions, such as toluene ($C_6H_5CH_3$) and benzene (C_6H_6), at different temperatures and preparation conditions was performed.

The dissolution kinetics in these solutions can be easily traced via UV-Vis, due to absence of any solvatochromic effects. The samples were prepared at different temperatures and conditions. Measurements were performed using UV-Vis Nano-spectrometer P360. The current concentration values of fullerenes in solution were obtained from measured absorption spectra using Lamber-Beer Law.

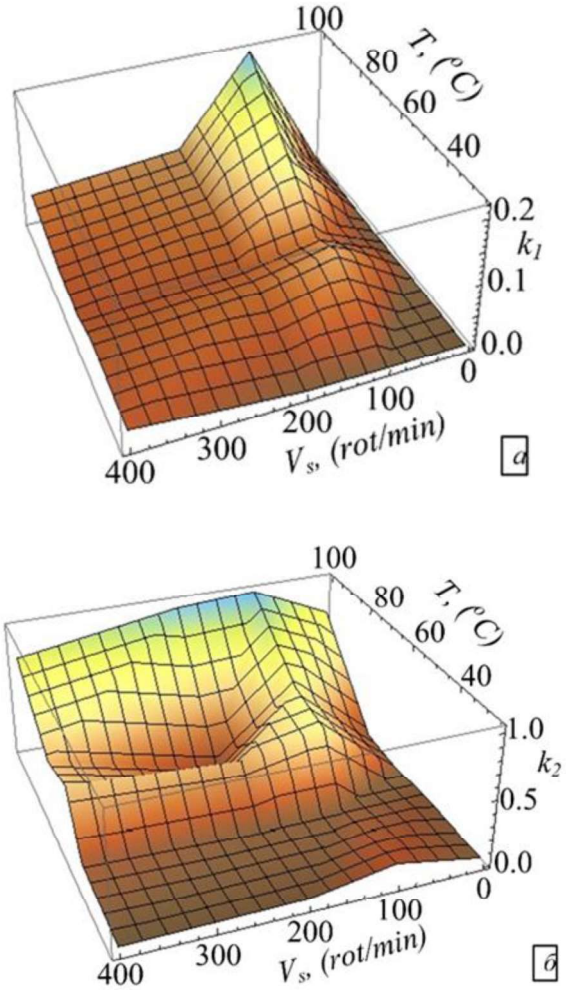

Figure 4. Dependence of the dissolution rate k_1 and the complex formation rate k_2 on the stirring speed and temperatures for C_{60}/NMP solution.

Using these results, the evolution of the concentration of C_{60} solutions in toluene and benzene was obtained for different temperatures and

stirring rates. To analyze the kinetics of dissolution, the equation of Noyes and Whitney was applied [8]:

$$\frac{dx}{dt} = C(S - x) \quad (2)$$

where x is the current concentration of the solution, S is the saturation concentration or the maximum concentration of fullerene, C is the dissolution constant.

It is shown that the dissolution is well described by the Noyes-Whitney expression and the dissolution parameters were determined.

For C_{60}/NMP solution, the dissolution equations should be extended by additional kinetic coefficient to account the complex formation. Therefore, kinetic equations were changed in the following way:

$$\begin{cases} \frac{dc(t)}{dt} = k_1(C_s - c(t)) \\ \frac{dy(t)}{dt} = k_2(c(t) - y(t)) \end{cases} \quad (3)$$

In (3), *c(t)* is the concentration of the "free" fullerene molecules in the solution, *y(t)* is the concentration of the C_{60}-NMP complexes in the system, C_s is the saturation concentration of C_{60}.

In the result, we obtained dependence of dissolution and complex formation coefficients on preparation conditions.

4. RESULTS AND DISCUSSION

In this work we have considered a theoretical model for description of cluster growth in C_{60}/NMP solutions. The stationary distribution functions were calculated and used for modeling of the small angle neutron scattering curves. The results of spectral analysis give cluster sizes of fullerene in NMP solutions at range 3.5-100 nm.

Investigations of kinetics of fullerene dissolution and complex formation were performed for low-polar and polar solvents at different preparation conditions. For low-polar solutions, the dissolution is well described by Noyes-Whitney equation. For polar solutions we had to extend dissolution equations to account for the complex formation. The dependence of kinetic parameters on different preparation conditions was obtained.

Investigation of structural properties of C_{70} in CS_2 solutions was performed at the SANS instrument in FLNP JINR, Dubna. The solutions were prepared at different conditions. The experimental results were compared to measurements by other groups.

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