Neutron studies of paramagnetic fullerene’s assembly in aqueous solutions

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Abstract. Recent results on structural studies of aqueous solutions of water-soluble derivatives of endofullerenes encapsulating 4f- and 3d-elements have been presented. Neutron small angle scattering experiments allowed recognize subtle features of fullerene’s assembly as dependent on chemical nature (atomic number) of interior atom, pH-factor and temperature of solutions. It was observed a fractal-type fullerene’s ordering at the scale of correlation radii ~ 10-20 nm when molecules with iron atoms are integrated into branched structures at low concentrations ($C \leq 1$ % wt.) and organized into globular aggregates at higher amounts ($C > 1$ % wt.). On the other hand, for Lanthanides captured in carbon cages the supramolecular structures are mostly globular and have larger gyration radii ~ 30 nm. They demonstrated a good stability in acidic ($pH \sim 3$) and neutral ($pH \sim 7$) media that is important for forthcoming medical applications.

1. Introduction

Since the discovery of La-endofullerenes [1] there is a growing interest in their synthesis and investigation of physical and chemical properties assuming also various biomedical applications, e.g. as Magneto-Resonance Imaging agents or antitumor preparations [2,3]. The unique endofullerenes’ feature which is very attractive for medicine is a durable encapsulation of heavy metal atoms inside a carbon cage which is strongly resistant against chemical attacks in living organisms. These integrated atoms do not release out of cages that prevent a contamination of biological tissues. At the same time, such isolated atoms retain their native properties, e.g. magnetic ones creating high relaxation rates of surrounding protons in biological media and this stimulates a search of ways to limit or regulate possible aggregation (clustering) to prevent irreversible sedimentation. The aim of this work is a comparative study of endofullerenols’ solutions ordering when their molecules contain 4f- or 3d-elements.

2. Experimental

Two series of fullerenols have been used [5,6]. The first group of the samples has included iron based endofullerenols Fe@C$_{60}$(OH)$_X$ ($X \sim 30$) (Fig.1) prepared by the process of hydroxylation of Fe@C$_{60}$ endofullerenes synthesized in electric-arc in inert atmosphere (helium) by the evaporation of composite electrodes (mixture of graphite and iron phthalocyanine pyrolysate).

Figure 1. Schematic view of iron endofullerenol Fe@C$_{60}$(OH)$_X$. 
In small angle neutron scattering experiments the crucial features of iron fullerenols self-assembly in aqueous solutions have been studied (“YuMO”-spectrometer, JINR, Dubna) for the concentrations $C = 0.25$-$2.0$ % wt. at ambient ($20^\circ$C) and enhanced temperature ($37^\circ$C, physiological conditions). In the experiments it was varied the pH value ($pH \sim 3$, fullerenols in pure water; $pH \sim 7$, phosphate buffer) to detect expected fullerenols’ local ordering which can be regulated in this way.

The second group gathered fullerenols $M@C_{2n}(OH)_Y$ ($Y \sim 40$) with 4f-elements ($M = Pr, Sm, Eu, Gd, Tb, Dy, Ho, Tm$). These substances contained of 5-10 % wt. of metal, and their carbon cages $C_{2n}$ were mainly $C_{82}$. The presence of higher fullerenes ($2n > 82$) was negligible since in the soot their amount was detected of 1.5 % wt. only.

In general it was used a common procedure of samples’ preparation. All fullerene-based structures embedded in the soot produced in electric arc then were extracted by the solvent (dimethylformamide) with a special catalyst addition. The soluble substances served for a production of fullerenols in the reaction of hydroxylation by hydrogen peroxide. Finally the mixtures of fullerenols were purified from the solvent traces during a double process of recrystallisation.

The chemical structure of fullerenols has been tested by IR-spectroscopy which confirmed OH-groups’ bonding to carbon cages. All the molecules of fullerenols have had the number of hydroxyls of $\sim 30$-$40$ that provided their good solubility in light water. The aqueous solutions possessed of $pH \sim 3.7$-$4.2$ (acidic media) weakly dependent on atomic number of captured metal atom. It means a cleavage of protons from the molecules which got a negative charge. Nevertheless, electrostatic repulsive forces did not prevent fullerenols’ aggregation of in various forms observed by small angle neutron scattering (SANS-Membrane, NRC KI – PNPI). Additionally the Atomic Force Microscopy (set up Solverbio, NT-MDT, semi-contact regime, probe NSG03) has been applied to visualize immediately a formation of fullerenols’ supramolecular structures. Very diluted solutions ($C \sim 10^{-2}$ % wt.) were deposited on polycrystalline Si, then dried and rinsed.

3. Discussion

SANS-data for iron fullerenols’ aqueous solutions qualitatively are similar at different conditions ($C, pH, temperature$). For illustration the spectra for these samples at ambient temperature and $pH \sim 7$ are shown only (Fig.2).

![SANS-patterns for iron fullerenols aqueous solutions (20°C, pH ~ 7) for the concentrations C = 2.0, 1.5, 1.0, 0.5, 0.25 % wt. (1-5).](image)

At low momentum transfers $q < 1$ nm$^{-1}$ the samples demonstrate a high increase of cross sections, by three orders in magnitude. It indicates a strong clustering in diluted and more concentrated systems that is described by the scattering function

$$d\Sigma/d\Omega = I_0[1 + (qR_C)^2]^{D/2} + B_g.$$  \hspace{1cm} (1)
The fitting parameters $I_0, R_C, D$ denote forward cross section, correlation radius and fractal dimension of observed structures, and incoherent background is presented by the parameter $B_g \approx \text{const}$. The magnitude of $I_0 \sim C$ increases proportionally to the concentration. It shows almost stable local ordering fullerenols in the concentration range $C = 0.25\text{ - }2.0 \text{ % wt.}$ As it was found from the estimates of scattering ability of fullerenols, the aggregation numbers in solutions achieve the magnitudes of $\sim 10^4$ at spatial scale of $R_C \sim 10\text{ - }20 \text{ nm}$ (Fig.3). With the increase of concentration in neutral medium ($pH \sim 7$) it was observed a progressive growth of the radii $R_C(C) \sim 11\text{ - }15 \text{ nm}$ as a result of structural transformation when branched aggregates (fractal dimension $D \sim 2.5 < 3$) become of globular type ($3 < D < 4$) (Fig.3). These trends are revealed also in acidic medium ($pH \sim 3$) where the formation of aggregates is still more pronounced and they are greater, $R_C \sim 20 \text{ nm}$ (Fig.4).

A comparative analysis of scattering data for iron fullerenols in solutions at different conditions (neutral or acidic medium, 20°C and 37°C) has testified on relatively stable scale of molecular self-assembly by a transition from diluted to moderately concentrated systems when it was observed only a densification of branched structures which became globular entities.
In following experiments another specific features in the local ordering of fullerenols due to the presence of 4f-elements (Pr, Sm, Eu, Gd, Tb, Dy, Ho, Tm) revealed at fixed concentration in solution (C = 1.5 % wt.). The data allowed understand in which way a variation of atomic numbers of metals (Z = 59-69) has modified fullerenols’ assembly. For fullerenols with Lanthanides the SANS-data transformed into the correlation functions γ(R) exhibited qualitatively similar patterns of \( P(R) = R^2 \gamma(R) \) in the range of radii \( R = 0-90 \) nm (Fig.5).

Figure 5. Fullerenols M@C_{82}(OH)X (X ~ 38-40) with 4f-metals (Pr, Sm, Eu, Gd, Tb, Dy, Ho, Tm). Spectra \( P(R) \) for aqueous solutions: concentration 1.5 % wt., ambient temperature (20°C), pH = 3.

A typical set of spectra \( P(R) \) is presented for fullerenols in pure water (pH ~ 3) at ambient temperature (20°C). The increase of temperature up to 37°C and transfer to neutral conditions (pH ~ 7) did not cause any substantial structural changes in fullerenols’ assembly. All the spectra for fullerenols captured the elements in the diapason of atomic numbers Z = 59-69 have exhibited qualitatively similar maxima in the spatial interval of \( R = 0-90 \) nm. The most intense peak located at \( R_m \sim 15-20 \) nm indicates a characteristic radii of aggregates.

The row of rare earth fullerenols demonstrates a common scale of molecular order in aqueous solutions. Fine structural features of the ordering of molecules with different metals inside are imprinted in the behavior of average gyration radii \( R_g(Z) \) (Fig.5, inset). It gets a maximum for Gd-fullerenols which possess the most pronounced paramagnetic properties of fundamental and practical interest for MRI (Fig.5). On the other hand, in the row of Lanthanides it was observed a substantial dispersion in aggregation degrees \( ~ 10^3 - 10^4 \) those are in the amplitudes of spectral maxima. The lowest ability to form nanostructures was detected for Eu-fullerenols, and the highest one was found for Samarium-based endohedral molecules, while in the case of captured Gadolinium it was observed a moderate aggregation (Fig.5).
4. Summary

A comprehensive SANS-analysis of the forms of molecular ordering for different kinds of fullerenols encapsulated 3d- or 4f-elements has elucidated really common features of molecular assembly observed as a formation of branched or globular superstructures relatively stable by a variation of pH-factor at ambient or physiological temperature. This demonstrates a universal character of fullerenols’ interactions in aqueous solutions which structuring is governed mainly by hydrogen bonds between hydroxyl-shells around carbon cages while a variation of chemical nature of metal inside a cage induces relatively weak effects in fullerenols’ interaction, e.g. due to electric or magnetic dipolar forces like in the case of Gd-fullerenols which showed a maximum gyration radius of aggregates among the structures with different Lanthanides.

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