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Neutron studies of paramagnetic fullerenols' 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 fullerenols assembly as dependent on chemical nature (atomic number) of interior atom, pH-factor and temperature of solutions. It was observed a fractal-type fullerenols' 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 medium where (MRI-diagnostics) [4]. On the other hand, a key problem of successful biomedical application of endometallofullerenes (EMF) is related to providing their solubility in aqueous 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 $\text{Fe@C}_{60}(\text{OH})_X$ ($X \sim 30$) (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).

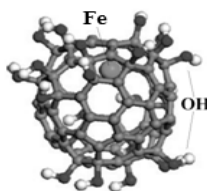


Figure 1. Schematic view of iron endofullerenol $\text{Fe@C}_{60}(\text{OH})_X$.



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 $C = 0.25\text{--}2.0$ % wt. at ambient (20°C) and enhanced temperature (37°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 ($M = \text{Pr, Sm, Eu, Gd, Tb, Dy, Ho, Tm}$). 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 $\sim 30\text{--}40$ that provided their good solubility in light water. The aqueous solutions possessed of $pH \sim 3.7\text{--}4.2$ (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).

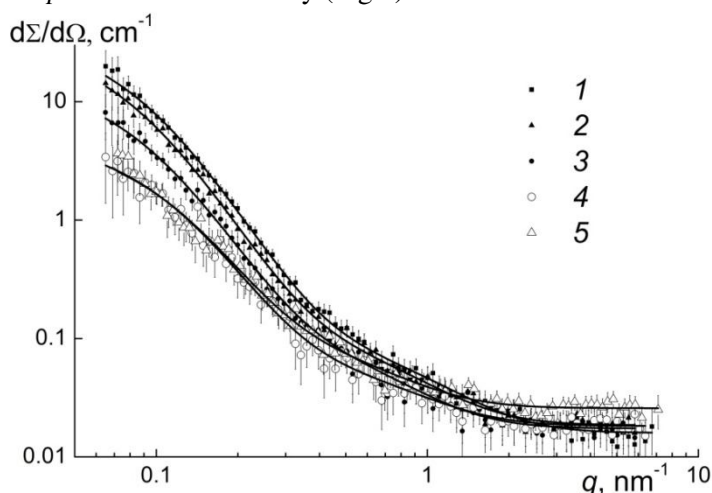


Figure 2. SANS-patterns for iron fullerenols aqueous solutions (20°C , $pH \sim 7$) for the concentrations $C = 2.0, 1.5, 1.0, 0.5, 0.25$ % wt. (1-5).

At low momentum transfers $q < 1 \text{ nm}^{-1}$ 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

$$d\Sigma/d\Omega = I_0/[1 + (qR_C)^2]^{D/2} + Bg. \quad (1)$$

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 $Bg \approx \text{const}$. The magnitude of $I_0 \sim C$ increases proportionally to the concentration. It shows almost stable local ordering fullerenols in the concentration range $C = 0.25\text{--}2.0$ % 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 $R_C \sim 10\text{--}20$ nm (Fig.3). With the increase of concentration in neutral medium ($pH \sim 7$) it was observed a progressive growth of the radii $R_C(C) \sim 11\text{--}15$ 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, $R_C \sim 20$ nm (Fig.4).

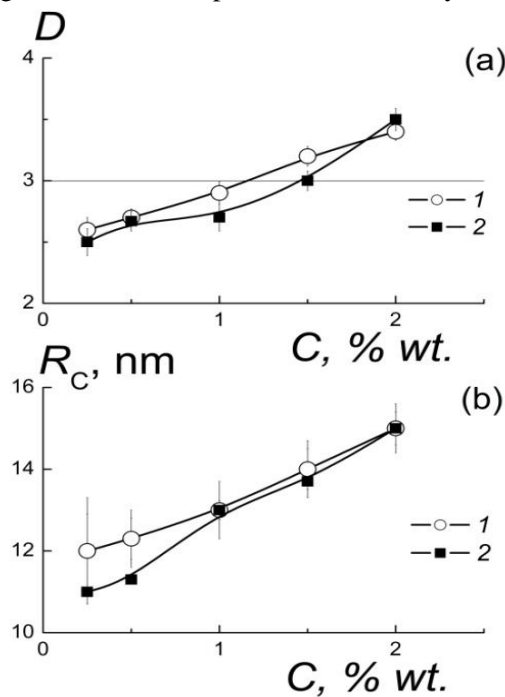


Figure 3. Fractal dimension $D(C)$ and correlation radius $R_C(C)$ (a,b) of fullerenols' structures vs. concentration in solutions ($pH \sim 7$) at 20°C and 37°C (1,2).

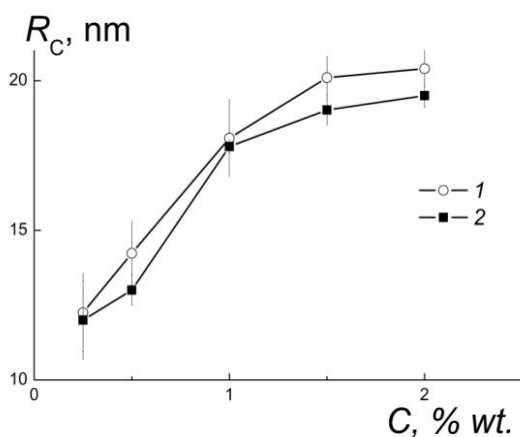


Figure 4. Correlation radius $R_C(C)$ of fullerenols' structures vs. content in solutions ($pH \sim 3$) at 20°C and 37°C (1,2).

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 $\gamma(R)$ exhibited qualitatively similar patterns of $P(R) = R^2\gamma(R)$ in the range of radii $R = 0-90$ nm (Fig.5).

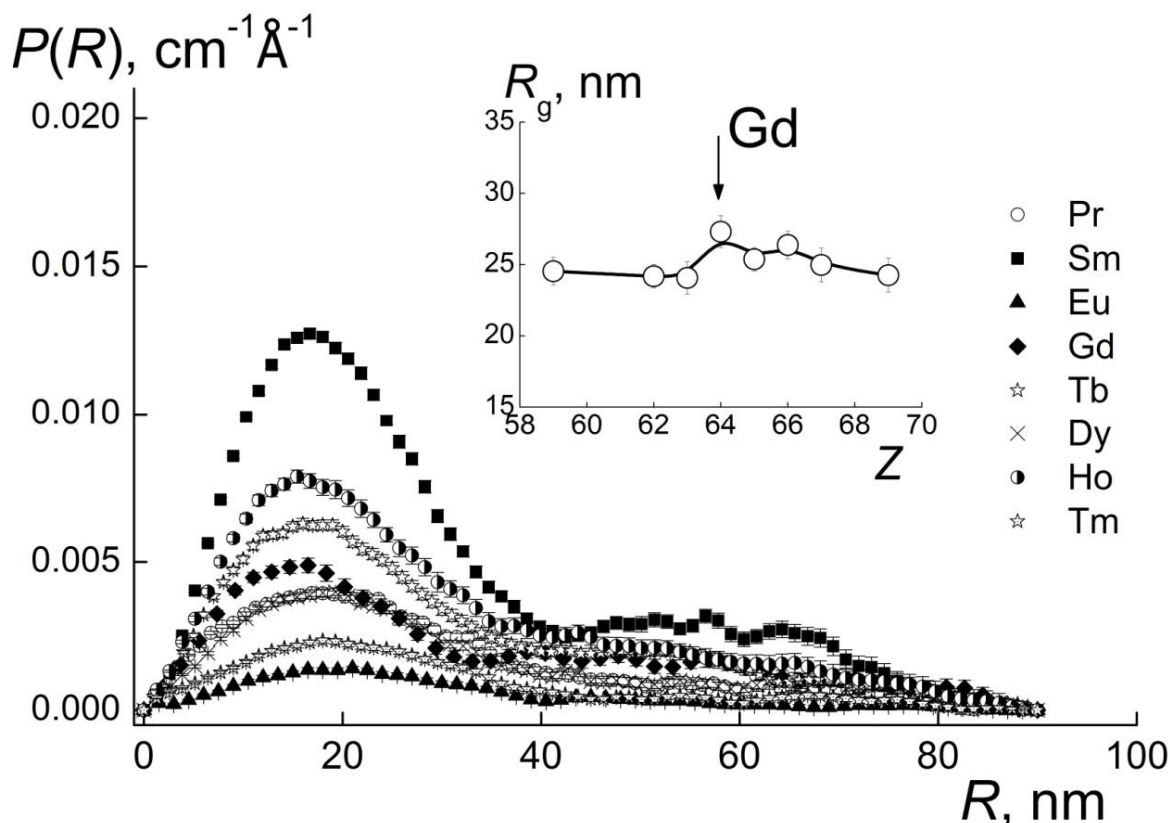


Figure 5. Fullerenols $M@C_{82}(OH)_x$ ($X \sim 38-40$) with 4f-metals (Pr, Sm, Eu, Gd, Tb, Dy, Ho, Tm). Spectra $P(R)$ for aqueous solutions: concentration 1.5 % wt., ambient temperature (20°C), $pH = 3$.

A typical set of spectra $P(R)$ is presented for fullerenols in pure water ($pH \sim 3$) at ambient temperature (20°C). The increase of temperature up to 37°C and transfer to neutral conditions ($pH \sim 7$) 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 $\sim 10^3-10^4$ 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.

Acknowledgement

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