Molecular characteristics of water-insoluble amino acid derivatives of [60]fullerene

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Molecular characteristics of solutions of ω-aminocaproic and *p*-aminobenzoic derivatives of [60]fullerene in DMSO have been studied by the diffusion method; it has been shown that the molecules form aggregates even in dilute solutions, the degree of aggregation being appreciably dependent both on the nature of the amino acid residue and on the concentration of the solution.

Recently, it has been shown by electron microscopy and by the diffusion method that water-soluble amino acid and peptide derivatives of [60]fullerene form aggregates in aqueous solutions, the degree of aggregation depending both on the concentration of the substance and on the nature of the amino acid or peptide fragments.[1–3] A series of aminocaproic acid derivatives of fullerene such as derivatives of aminobenzoic and amino acids and of proline are insoluble in water but are soluble in some organic solvents such as pyridine, dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). Free fullerene is insoluble in these solvents.

It may be suggested that solutions of amino acid derivatives of fullerene in organic solvents, similarly to aqueous solutions of these compounds, contain molecular aggregates. In this paper, we studied DMSO solutions of the fullerene derivatives of *p*-aminobenzoic **1** and ω-aminocaproic **2** acids of general formula ($HC_{60}NHXCO_2H$).

To study the molecular characteristics of these solutions, we used data from measurements of the diffusion coefficient D.[4] The experiments were carried out on an MOM-3180 analytical ultracentrifuge (Hungary) using Philpot–Svennson optics at a rotor temperature of 25±0.1 °C. DMSO was used as the solvent, and the concentration varied in the range 0.07–0.15 g dm^{-3} (higher concentrations afford too dark, non-transparent solutions, whereas lower concentrations cannot be studied due to an insufficient increment in the refraction index). Measurements of the diffusion coefficients (D) were carried out in a boundary-forming cell by layering the solvent onto a solution of finite concentration falling within the concentration range mentioned above. Pictures of the boundary between the pure solvent and the solution were taken at regular intervals, and its broadening was thus monitored. The rotation frequency of the rotor (4000 rpm) was chosen in such a way that sedimentation of the particles did not occur during the experiment, and the boundary broadened only due to the diffusion. It is known that from diffusion coefficients measured in solution, the coefficients of forward friction of molecules and their average hydrodynamic radius, the so-called Stokes radius, can be calculated. If molecules of the compounds under investigation exist in solution as spheres and are not solvated, one can easily pass from the Stokes radius to the volume of the particles and to their molecular mass.[5] In addition, the known diffusion coefficient makes it possible to monitor the stability of the molecular structure and its possible variations in solution. The partial specific volume of particles in the solution, v, was determined by pycnometry. Using the diffusion coefficients D_c and the partial specific volumes of particles v determined experimentally and the equations reported previously,[2] we calculated the forward friction coefficients f, molecular masses M of particles (we called them aggregates), the number of individual molecules with molecular mass M_0 in an aggregate $n = M/M_0$, the volumes of aggregates and of individual molecules $V_{agg} = V_{sph}$ and $V_0 = V_{agg}/n$, as well as their diameters $d_{agg} = d_{sph}$ and $d_0 = (6V_0/\pi)^{1/3}$. The results of the calculations are presented in Table 1.

It can clearly be seen from Table 1 that in DMSO compounds **1** and **2** form aggregates even at low concentrations. In the case of **1**, the measurements were carried out over a very narrow concentration range but even within this range, as the concentration decreased from 0.09 to 0.07 g dm^{-3}, the degree of aggregation decreased by a factor of approximately three. The degree of aggregation for compound **1** is not very high and varies from several molecules to several tens of molecules. However, it may be suggested that the degree of aggregation would rapidly increase with an increase in the concentration of the solution. This is supported by electron microscopy data, which imply that the compound **1** forms large aggregates[6] in pyridine or in DMSO at higher concentrations. As regards compound **2**, the results of measurements of the diffusion coefficients indicate that this compound exists as large particles consisting of several hundreds of molecules even in highly dilute solutions. A twofold increase in the concentration of the solution results in a six-fold increase in the degree of aggregation. In this case, the presence of large aggregates was also confirmed by electron microscopy, which showed that large conglomerates occur in solutions of the compound **2** in pyridine or DMSO.[6]

Our studies permit the following conclusions to be drawn:

(1) amino acid derivatives of fullerene form molecular aggregates in organic solvents;

(2) the degree of aggregation depends appreciably on the concentration of the solution and on the nature of the amino acid fragment.

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Table 1 Molecular characteristics and sizes of the aggregates of molecules of water-insoluble fullerene derivatives of amino acids measured in dimethyl sulfoxide ($\eta_0 = 20.1\times10^{-1}$ Poise).

C /g dm^{-3}	$D/10^{-7}$ cm^2 s^{-1}	$f/10^{-8}$ g s^{-1}	M/Da	n	V_{agg}/A^3	V_0/A^3	d_{agg}/A	d_0/A
	N-(Monohydrofullerenyl)-*p*-aminobenzoic acid (M_0 = 857; V = 0.382 cm^3 g^{-1})							
0.090	8.0	5.14	16570	19.3	10536	546	27.2	10.10
0.080	8.9	4.62	11960	14.0	7606	545	24.4	10.13
0.070	11.3	3.64	5830	6.8	3706	545	19.2	10.14
	N-(Monohydrofullerenyl)-ω-aminocaproic acid (M_0 = 851; V = 0.500 cm^3 g^{-1})							
0.150	1.5	28.44	2135000	2508.8	1772000	706.3	150.1	11.05
0.125	2.3	17.72	516000	606.0	428540	707.2	93.5	11.05
0.075	2.6	16.05	383000	450.0	318440	707.6	84.8	11.05

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