PROTON-PROTON SPIN RELAXATION IN ORGANIC SOLVENTS CONTAINING FULLERITE C_{60} NANOSTRUCTURES

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The experimental data concerning nuclear spin-spin relaxation for protons in different pure organic solvents as well as for protons in solutions containing fullerite C_{60} nanostructures are presented. It is known that fullerite is not dissolved in such polar solvents as alcohol, acetone, tetrahydrofuran and others. It is weak dissolved in pentane, hexane and decane. But fullerite is well dissolved in such solvents for which the value of the specific enthalpy related to the specific volume of the dissolvent molecule is near to corresponding value for C_{60} fullerene molecule.

Clusterization of Fullerene C_{60} Molecules in Solutions

The important peculiarity of fullerenes in solutions is their clusterization with formation of $(C_{60})_n$ aggregates where *n* is the number of fullerene molecules which are contained in the fullerene aggregate. This number depends on many factors such as type of solvents, concentration of fullerene molecules in solutions, temperature, etc. The existence of fullerene $(C_{60})_n$ aggregates in solutions was demonstrated by osmometric data (fullerenes in toluene and chlorobenzene [1]), non linear optics data (fullerenes in benzene [2]) and light diffusion data (fullerenes in benzene [3]).

Drop Model. In the drop model of fullerene aggregates the values of *n* are estimated in limits from *n*=3 (at T=190K) to *n*=11 (at T=380K) [4]. According to Ref. [4] at the increase of temperature up to 380K the number of fullerene molecules in $(C_{60})_n$ fullerene aggregates does not change. Therefore we can consider that at room temperature these aggregates represent the fullerite nanostructures in solution with pronounced solid state properties.

However, the drop model used usually for description of the thermodynamic characteristics of fullerene clusters in solutions must be precised. It follows from the light diffision experimental data [3]. According to these data the overage dimension of fullerene C_{60} aggregates in solution changes continuously during long time (about 50 days). If the vessel with fullerene clusters containing solution to shake slightly than the clusters are wrecked. But after very short time the process of clusters formation repeated again. The clusters have a fractal structure with the fractal dimension equal to 2,9. The existence of the fractal structure of the fullerene aggregates in organic solvents leads to changing of the estimated above number of the fullerene C_{60} molecules in fullerene clusters which has obtained in simple drop model of clusterization.

EXPERIMENTAL

The values of nuclear spin-spin relaxation time T_2 in different protons containing systems were obtained by means of Hahn spin echo method. The values of T_2 at room temperature for organic solvents toluene, xylene, chlorobenzene and brombenzene without fullerite C_{60} nanostructures are presented in the Table I. The dependence of T_2 values on the type of solvents is caused by difference in configuration of protons in molecules.

Table I. The values of proton-proton spin relaxation times T_2 in organic solvents.

The solvent	T_2, ms
toluene, $C_6H_5CH_3$	39,5
xylene, $C_6H_4(CH)_2$	45,1
chlorbenzene, C_6H_5Cl	53,3
brombenzene, C_6H_5Br	46,0

In the Table II the values of proton-proton spin relaxation times T_2 at room temperature in the same organic solvents containing fullerite C_{60} nanostructures in form of giant fullerene clusters are presented.

Table II. The values of proton-proton spin relaxation times T_2 in organic solvents containing fullerite C_{60} nanostructures.

The solution	Concentration of C_{60}, mg/ml	T_2, ms
$C_6H_5CH_3{:}C_{60}$	2,8	36,1
$C_6H_4(CH)_2{:}C_{60}$	5,2	39,5
$C_6H_5Cl{:}C_{60}$	7,0	45,6
$C_6H_5Br{:}C_{60}$	3,3	43,6

The concentrations of the fullerene C_{60} molecules given in the Table II correspond to the limit of solubility of the fullerite in the investigated solutions. We see that presence of fullerene aggregates formed by C_{60} molecules in each of these solutions leads to decreasing of the nuclear spin-spin relaxation time T_2 of hydrogen nuclei. Such effect indicated that in presence of fullerene clusters $(C_{60})_n$ the new cannel of nuclear spin-spin relaxation is opened. As it is known [5] for fullerene C_{60} molecule the NMR signal at 143 ppm is characteristic. But the spins of carbon nuclei cannot change essentially the proton-proton spin relaxation rate as consequence of weak interaction between solvent protons and carbon nuclei spins. Therefore the influence of fullerite C_{60} nanostructures on nuclear spin-spin relaxation in organic solvents is caused by existence in solution of a stable C_{60}^{1-}, C_{60}^{2-} and, possibly, C_{60}^{3-} ions [5]. The presence of these stable ions on surface of fullerene C_{60} nanostructures leads to its interaction with nuclear spins of the solvent. As result of this interaction the supplementary fluctuating magnetic field arises. This field causes additional contribution into processes of the nuclear spin-spin relaxation via paramagnetic centers.

Diffusion of Fullerene C_{60} Aggregates

The average dimensions of fullerene aggregates in solutions are dependent on its concentration. This leads to concentration dependence of diffusion coefficients. Namely, the diffusion coefficients of fullerenes in saturated solutions are about 30% smaller comparatively with corresponding values for separate fullerene molecules. This is caused by formation of the clusters from fullerene molecules.

The increase of proton-proton spin relaxation rate at interaction of proton spins with negative fullerene ions taking into account fullerene C_{60} aggregates is discussed.

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