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**EFFECT OF FULLERENE C<sub>60</sub> ON THE DIFFUSION  
OF ORGANIC SOLVENTS' MOLECULES**

The results of studying the dynamics of molecules of solutions of fullerene C<sub>60</sub> in benzene and toluene are presented. The studies were carried out by the method of quasi-elastic scattering of slow neutrons. The following were determined: the total self-diffusion coefficient  $D$ , its collective  $D_{\text{coll}}$  and single-particle  $D_{\text{s-p}}$  contributions, and molecule relaxation time  $\tau_0$  before and after the dissolution of fullerene. It is necessary to pay attention to the fact that in our case a kind of neutron contrast experiment takes place. The significant difference (more than ten times) in the cross-sections for an incoherent scattering of neutrons by hydrogen and carbon nuclei made it possible to obtain diffusion parameters that characterize the dynamics of solvent molecules exclusively. It turned out that the intensity of diffusion movements of solvent molecules is almost ten times higher than the mobility of fullerene molecules.

*Keywords:* fullerenes, quasi-elastic scattering of slow neutrons, self-diffusion coefficient, single-particle and collective components of the self-diffusion coefficient.

**1. Introduction**

The study of dynamic processes in fullerene solutions is an important task both from the point of view of fundamental science and from a versatile applied application. The peculiarity of fullerene molecules' structure determines their unique physical and chemical properties and wide practical application: from the latest nanotechnologies to biology and nanomedicine [1, 2]. Modern methods of obtaining and purifying fullerenes in macroscopic quantities are based on dissolution technology. Due to the intense thermal effect on the surface of crystalline graphite, soot is formed, which contains up to 12 % fullerenes. The separation of fullerenes from soot is based on the fact that, unlike soot, fullerenes are quite soluble in benzene, toluene, xylene and other organic solvents [1]. Studies have established the complex nature of the behavior of the structural, electrical and optical properties of fullerene solutions, which is due to their cluster nature. Changes in the structure of the organic solvent in the presence of C<sub>60</sub> fullerene cause the appearance of peculiarities in its kinetic properties, in particular, in the solvent self-diffusion coefficient.

We should also note that toluene differs from benzene by only one methyl group, CH<sub>3</sub>. Thus, we have the opportunity to identify the role of this group in dynamic processes. Therefore, the aim of this work was to study by neutron spectroscopy the effect of C<sub>60</sub> fullerene on the dynamics of molecules of organic solvents.

**2. Samples preparation and research method**

Fullerenes were extracted with a soot solvent. Soot was obtained in the process of electric arc evaporation of graphite electrodes and subsequent condensation of carbon atoms in a helium atmosphere. The yield of fullerenes was about 10 %, and C<sub>60</sub> fullerenes were formed, based on the extraction data, almost three times more than C<sub>70</sub>. The solid residue of soot was easily separated by filtration, after which the solutions were used in neutron scattering experiments. By the way, powdered fullerenes were easily obtained by evacuating solutions with heating to 423 K, after which they could be redissolved in another solvent. In the experiments, we used samples of C<sub>60</sub> solutions in benzene and toluene with a concentration of 3 mg/l and pure solvents (benzene and toluene). This was done in order to avoid the formation of associates of fullerene molecules and precipitation.

The research was carried out by the method of quasi-elastic slow neutron scattering (QENS) [3], the essence of which is that neutrons, interacting with the diffusion motions of molecules, change their energy and momentum in the process of scattering. This leads to the broadening of the monochromatic line of neutrons incident on the sample. Information on the diffusion characteristics is contained in the functional dependence of this energy broadening on the neutron momentum change square during its scattering. The methodology and calculation procedure are presented in detail in [3].

To interpret the QENS spectra, the model presented in [3] was used, in which the self-diffusion of water molecules is carried out by two mechanisms: 1) the mechanism of continuous diffusion: the molecule oscillates during time  $\tau_0$  in the environment of its neighbors, namely the environment is continuously moving in space; 2) activation mechanism of diffusion: the molecule after a time  $\tau_0$  jumps to another environment, and there continues to oscillate until a new jump. That is, the energetic expansion of the quasi-elastic peak in liquids can be represented as the sum of the collective and single-particle contributions. This, in turn, allows the total self-diffusion coefficient to be decomposed into two components: collective and single-particle.

Thus, the following are considered as characteristics of self-diffusion of molecules [3]:

$D$  – the total diffusion coefficient;

$D_{\text{coll}}$  – coefficient, reflecting the continuous mechanism's contribution to the total diffusion coefficient of molecules. It describes collective movements;

$D_{\text{s-p}}$  – single-particle component in the total diffusion coefficient;

$\tau_0$  – the time of the settled life of molecules in the equilibrium position;

$l_0$  – average jump length of a molecule;

$l$  – the average length of continuous movement of the molecule.

The study of the QENS spectra was carried out on a multidetector neutron spectrometer based on the time of flight of the WWR-M nuclear research reactor of the Institute for Nuclear Research of the National Academy of Sciences of Ukraine. The energy of neutrons incident on the sample is 13.2 meV. Scattered neutron spectra were measured in the range of angles  $25.1 - 101.3^\circ$  and recorded by the AI-9216 multivariate time analysis system [4]. The study sample was in a flat  $50 \times 60$  mm container with duralumin diaphragms 0.5 mm thick. The sample thickness was chosen equal to 0.9 mm to exclude the contribution of multiple neutron scattering to the spectra.

### 3. Research results and their discussion

Before proceeding with the analysis of experimental data, it is necessary to pay attention to the specifics of neutrons' interaction with molecules that contain hydrogen. The cross-section component for an incoherent scattering of neutrons by protons is  $\sim 10$  times higher than the cross-sections for scattering by other atoms' nuclei. Therefore, the dynamics of molecules of hydrogen-containing liquids are studied by the neutron method indirectly – through diffuse motions of hydrogen atoms. In our case, the

benzene molecule contains six hydrogen and carbon atoms, and the toluene molecule, respectively, seven and eight. The total cross-section for incoherent neutron scattering by a benzene molecule is  $\sim 15$  times larger than its coherent cross-section (carbon is a purely coherent scatterer). For a toluene molecule, this ratio is  $\sim 16$ . Therefore, considering the mass and size of the fullerene molecule and the ratio of the cross-sections for neutron scattering by carbon and hydrogen nuclei, the broadening of the QENS  $\Delta E(Q^2)$  peaks in our studies is caused practically by diffusion motions of exclusively organic solvent molecules. In other words, in our case, a kind of neutron-contrast experiment takes place, which made it possible to obtain diffusion parameters that characterize the dynamics of only solvent molecules.

Figs. 1 and 2 show the dependence  $\Delta E(Q^2)$ , respectively, for solutions of fullerene  $C_{60}$  in benzene and toluene.

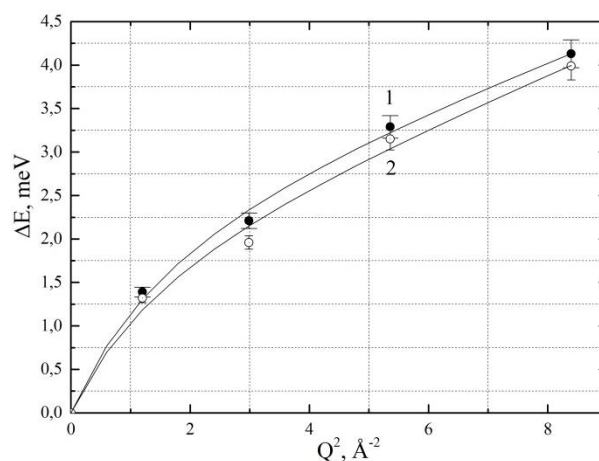


Fig. 1. Energy broadening of quasi-elastic peaks depending on the  $Q^2$  of benzene (1) and the benzene-fullerene  $C_{60}$  (2) system. Circles – experiment, solid lines – calculation.

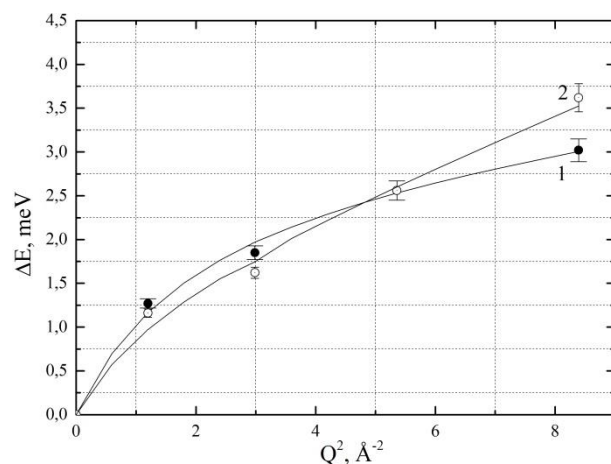


Fig. 2. Energy broadening of quasi-elastic peaks depending on  $Q^2$  of toluene (1) and toluene-fullerene  $C_{60}$  (2). Circles – experiment, solid lines – calculation.

You can see from these Figures that the  $\Delta E(Q^2)$  dependence is not linear either in pure organic solvents or in fullerene solutions. That is, in these substances, in addition to the collective one, there is also one-particle (activation) diffusion. However, for a toluene-fullerene solution, the energy dependence  $\Delta E(Q^2)$  is closer to linear (see Figs. 1 and 2). These figures also demonstrate that in a solution based on benzene, there is a slight decrease in the intensity of diffusion movements of solvent molecules. At the same time, in the toluene-fullerene system, there is a significant change in the mechanisms of diffusion movements of solvent molecules.

An important parameter characterizing molecules' behavior of fullerene solutions is the molecules' diffusion coefficient. It determines the optimal conditions for the crystallization of fullerenes in solutions and the possibility of their separation and purification. So, according to the procedure described in [3], the following were determined: the total self-diffusion coefficient  $D$ , its collective  $D_{\text{coll}}$  and single-particle  $D_{\text{s-p}}$  components and the relaxation time  $\tau_0$ , the jump length  $l_0$  of the molecule and the length of its movement by the mechanism of continuous diffusion  $l$  before and after the dissolution of fullerene. The values of these diffusion characteristics are given in Table.

**Diffusion parameters of pure benzene and toluene and in solutions with fullerene C<sub>60</sub>**

Sample	$D$ , $10^{-9} \text{ m}^2/\text{s}$	$D_{\text{coll}}$ , $10^{-9} \text{ m}^2/\text{s}$	$D_{\text{s-p}}$ , $10^{-9} \text{ m}^2/\text{s}$	$\tau_0$ , $10^{-12} \text{ s}$	$l_0$ , $10^{-10} \text{ m}$	$l$ , $10^{-10} \text{ m}$
Benzene	8.80 ( $\pm 0.4$ )	1.95 ( $\pm 0.1$ )	6.85 ( $\pm 0.3$ )	0.64 ( $\pm 0.03$ )	1.62 ( $\pm 0.08$ )	0.86 ( $\pm 0.04$ )
Benzene + fullerene	8.36 ( $\pm 0.4$ )	2.15 ( $\pm 0.1$ )	6.21 ( $\pm 0.3$ )	0.78 ( $\pm 0.04$ )	1.70 ( $\pm 0.08$ )	1.0 ( $\pm 0.05$ )
Toluene	8.04 ( $\pm 0.4$ )	0.81 ( $\pm 0.05$ )	7.23 ( $\pm 0.4$ )	0.59 ( $\pm 0.03$ )	1.61 ( $\pm 0.08$ )	0.54 ( $\pm 0.03$ )
Toluene + fullerene	7.35 ( $\pm 0.4$ )	2.17 ( $\pm 0.13$ )	5.18 ( $\pm 0.3$ )	1.29 ( $\pm 0.07$ )	1.87 ( $\pm 0.08$ )	1.21 ( $\pm 0.07$ )

From their analysis, it follows that, firstly, the total coefficient  $D$  of all objects of research is formed (by more than 70 %) by the activation mechanism of diffusion. Second, after the dissolution of C<sub>60</sub> fullerene, the total self-diffusion coefficient of benzene decreases by ~ 4 %, and for toluene by ~ 8.6 %. At the same time, the collective component of  $D_{\text{coll}}$  increases by 10 and 63 %, respectively. The single-particle  $D_{\text{s-p}}$  component of the total self-diffusion coefficient of molecules on going from a pure solvent to a solution, on the contrary, decreases by 9 and 28 %, respectively, for benzene and toluene. Thus, the dissolution of C<sub>60</sub> fullerene in an organic solvent causes a redistribution between the collective and single-particle components of the total self-diffusion coefficient and its decrease. These changes are accompanied by an increase in time  $\tau_0$  of molecule in the vibrational state, length of its jump  $l_0$ , and continuous movement  $l$ . As we see, fullerene C<sub>60</sub> significantly affects molecules' dynamics of the fullerene-toluene system. And this is due to the presence of the CH<sub>3</sub> methyl group in toluene, which increases the reactivity of the benzene ring.

As noted above, in the case of our samples, the QENS method provides information on diffusion and its mechanisms exclusively of solvent mole-

cules. In [5], the results of studying the diffusion of fullerene C<sub>60</sub> in benzene are presented. The total coefficient is  $9.1 \cdot 10^{-10} \text{ m}^2/\text{s}$ . That is, the intensity of diffusion movements of fullerene C<sub>60</sub> molecules in solution is ~ 10 times less than the intensity of diffusion of solvent molecules.

#### 4. Conclusions

The investigation by the QENS method made it possible to determine the diffusion characteristics of benzene and toluene molecules, both pure and in solutions with fullerene C<sub>60</sub>.

It was found that their total self-diffusion coefficient  $D$  is almost 10 times higher than that of fullerene molecules.

It is revealed that the total self-diffusion coefficient  $D$  is formed by more than 70 % by the activation mechanism of diffusion of solvent molecules.

When fullerene C<sub>60</sub> dissolves, a redistribution occurs between the activation and collective mechanisms of self-diffusion of solvent molecules and a decrease in the total coefficient  $D$ .

Although benzene and toluene structurally differ only in one methyl group CH<sub>3</sub>, the presence of this group causes significant changes in the dynamics of toluene molecules upon dissolution of fullerene C<sub>60</sub>.

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### ВПЛИВ ФУЛЕРЕНУ C<sub>60</sub> НА ДИФУЗИЮ МОЛЕКУЛ ОРГАНІЧНИХ РОЗЧИННИКІВ

Представлено результати дослідження динаміки молекул розчинів фулерену C<sub>60</sub> у бензолі і толуолі. Дослідження проводилися методом квазіпружного розсіяння повільних нейтронів. Було визначено повний коефіцієнт D самодифузії, його колективний D<sub>coll</sub> та одночастинковий D<sub>s-p</sub> внески та час осілого життя τ<sub>0</sub> молекули до і після розчинення фулерену. Установлено, що при розчиненні фулерену C<sub>60</sub> в органічному розчиннику відбувається перерозподіл між колективною і одночастинковою складовими повного коефіцієнта самодифузії молекул розчину, у результаті чого цей коефіцієнт самодифузії зменшується. Необхідно звернути увагу на те, що в нашому випадку має місце своєрідний нейтронно-контрастний експеримент. Велика різниця (більш ніж у 10 разів) у перерізах некогерентного розсіяння нейтронів на ядрах водню і вуглецю дозволила отримати параметри дифузії, що характеризують виключно динаміку молекул розчинника. Як виявилось, інтенсивність дифузійних рухів молекул розчинників майже у 10 разів перевищує рухливість молекул фулерену.

*Ключові слова:* фулерени, квазіпружне розсіяння повільних нейтронів, коефіцієнт самодифузії молекул, одночастинкова і колективна складові коефіцієнта самодифузії.

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