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STRUCTURE OF FULLERENE AGGREGATES IN PYRIDINE/WATER SOLUTIONS BY SMALL-ANGLE NEUTRON SCATTERING

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1. Introduction

The behavior of fullerenes in solutions is characterized by a number of specific effects [1]. One of them is the solvatochromism—a sharp change of the solution color with a small change in the solvent composition. In particular, it was reported [2], that the mauve color of solutions C_{60}/pyridine/water with the H_2O concentration less than 50 molar % changes to yellow when the H_2O concentration approaches 50%. This effect is assumed [2] to be connected with the formation of specific aggregates in solutions. The dynamic light scattering (DLS) study [2] pointed to the fact that these aggregates are rather monodisperse and have a spherical shape with the radius of about 30 nm. Chemical tests using hydrazine [2] revealed complete chemical inertness of C_{60} in these solutions. The latter testifies that C_{60} is covered by a pyridine shell protecting the surface of C_{60} against hydrazine. Fig.1 presents two possibile structures of the aggregates—pyridine covers a massive core consisting of C_{60} molecules (a) or pyridine covers one/several molecules of C_{60} and the aggregates consist of these combined particles (b).

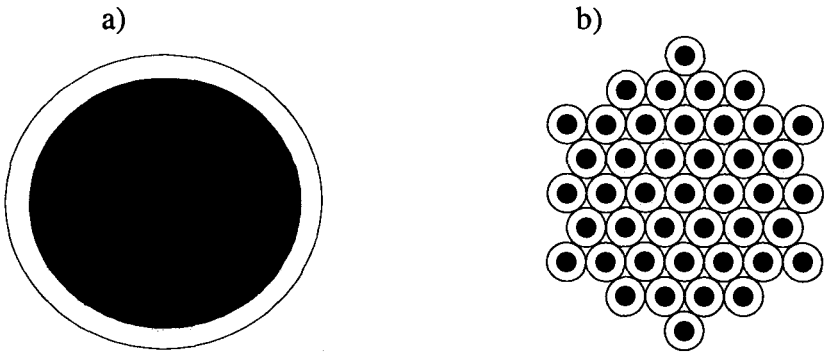


Figure 1. Schematic picture of possible structures of the C_{60} aggregates in pyridine/water solutions. Black cores and white shells correspond to C_{60} and pyridine, respectively.

The aim of the current work was to try the small-angle neutron scattering (SANS) for solving the inner structure of the discussed aggregates. The use of SANS for fullerene solutions faces a problem [3]. On the one hand, the protonated solvents have the high incoherent cross section, which does not make it possible to obtain scattering curves in a wide range of momentum transfer (q-vector). On the other hand, the deuterated solvents have virtually no scattering contrast with fullerenes. Nevertheless, for the considered solutions the estimates of the scattering, in assumption that the aggregate radius is less than 30 nm, show that the scattering curves differ significantly for different combinations of protonated/deuterated components (water and pyridine) at q-values less than 0.3 nm^{-1}. In the given report the results of SANS experiments in a q-range 0.08÷1 nm^{-1} are presented.

2. Materials and methods

C_{60} and pyridine (both 98% purity) were purchased in Hoecht and Merck, respectively. C_{60} was dissolved in pyridine with a concentration of 0.5 mg/ml (maximal solubility is 0.89 mg/ml [4]). Then, this solution was added to water up to the concentration of 10%. Hence, the total concentration of C_{60} in solutions was 0.05 mg/ml. The change in color from mauve for the C_{60}/pyridine solution to yellow for the final solution was observed in agreement with the previous work [2]. Four solutions with different combinations of deutareted/protonated water (H_2O/D_2O) and pyridine (H-Py/D-Py) were prepared. They were H-Py and D-Py in H_2O and D_2O, respectively.

Small-angle neutron scattering (SANS) experiments were carried out on SANS instruments at the Budapest Neutron Center (BNC), Hungary, and the pulsed neutron reactor IBR-2 of the Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Russia. At BNC, measurements were made at a fixed wavelength of 0.5 nm (resolution 13%) and a sample-detector

distance of 5.5 m covering a q-range 0.1÷0.6 nm^{-1}. The calibration was made using water with usual corrections [5]. At the IBR-2, the scattering curves were obtained over a wavelength interval 0.05÷0.5 nm^{-1} and at a sample-detector distance of 12 m covering a q-range 0.08÷2 nm^{-1}. The calibration was made by a special procedure using vanadium [6]. The temperature of the solutions was maintained at 20°C. As a buffer, the 10% pyridine aqueous solution was used. This buffer is quite correct due to the small content of C_{60} in the studied solutions. The estimates show that the effect of pyridine, which could be included into the aggregates, on the scattering density of the solvent is negligibly small.

3. Results and discussion

First experiments at BNC revealed a slight excess of the SANS signal of the solution over the buffer scattering. The scattering curve obtained for 12 hours in the case of D-Py in H_2O is presented in Fig.2. It is clear that the used instrumental regime does not allow us to obtain reliable SANS curves. Unfortunately, further increase of the neutron wavelength at the setup (i. e. decrease of the minimal q-value and increase of the q-resolution) results in a great loss of the incident intensity and, as a consequence, leads to insufficient signal-to-noise ratio. However, from the slight rise of the scattering at small q-values in Fig.2 one can estimate the radius of the inhomogeneities in the solution, which is less than 30 nm. Secondary peaks are not observable because of the small signal-to-noise ratio. The analysis of the full scattering over all detected angles for different combinations of the deutarated/protonated components of the studied solutions gives the following results. After the background is subtracted, the cases H-Py and D-Py in H_2O give ≅10% excess of the solution scattering over the buffer scattering. For the case H-Py in D_2O it is ≅ 5%, For the case H-Py in D_2O it is ≅ 5%, and in the case D-Py in D_2O there is virtually no difference between solution and buffer scattering (less than 1%).

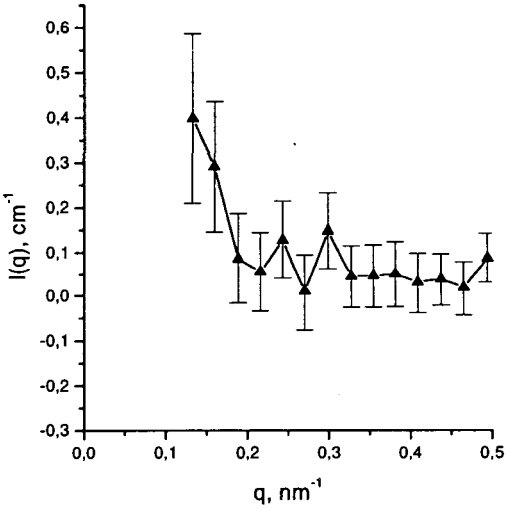
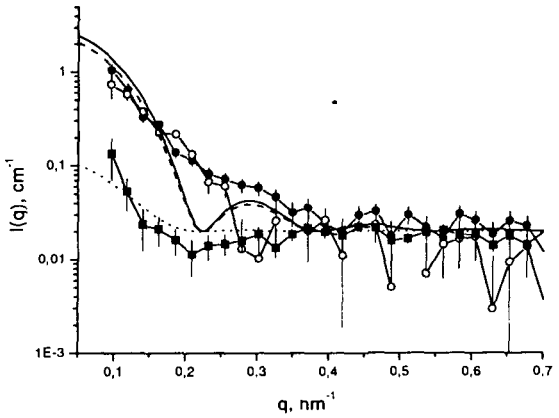


Figure 2. Scattering curve of the C_{60}/ D-Pyridine/H_2O solution (BNC).

Scattering curves obtained at the IBR-2 for one day are shown in Fig.3 (small-angle scattering for D-Pyridine in D_2O, like in previous experiments, were not observed). In the same figure one can see model calculations corresponding to two possible cases (Fig.1). In both cases the radius of the aggregates and the width of the pyridine shell are assumed to be 20 and 0.25 nm, respectively. In the second model the primary particles consist of one C_{60} molecule (radius 0.5 nm) covered by the pyridine shell. Qualitatively, one can conclude that the first model (Fig.1, a) fits the experimental data better. In other words, the comparison of the calculated and obtained scattering curves, as well as the relative position of the scattering curves corresponding to different combinations of deuterated/protonated solution components in absolute scale, points to the small pyridine content inside the aggregates. The further quantitative analysis to determine exact values of the C_{60} and pyridine content in the aggregates is not possible at the setup because of the insufficient resolution at q-values less than 0.2 nm^{-1}. The last fact also does not allow us to

a)



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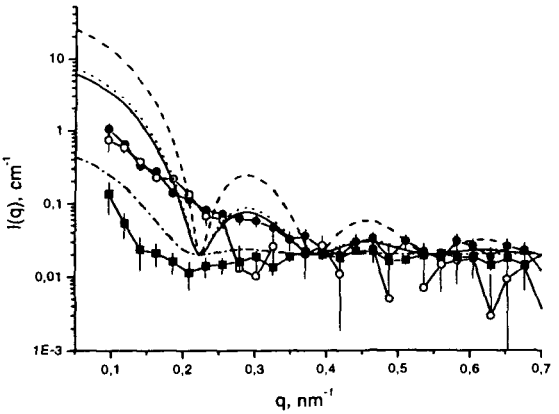

Figure 3. Experimental scattering curves of C_{60} (IBR-2) in different combinations of solvent (-•- H-Py / H_2O; -o- D-Py / H_2O; -■- H-Py / D_2O) together with calculated curves. The graphs contain the same experimental and different calculated curves.

a) Calculated curves (— H-Py / H_2O; - - - D-Py / H_2O; ····· H-Py / D_2O) correspond to model (a) in Fig.1.

b) Calculated curves (— H-Py / H_2O; - - - D-Py / H_2O; ····· H-Py / D_2O; -·-·- D-Py / D_2O) correspond to model (b) in Fig.1.

make a reliable conclusion about the rate of the polydispersity of the detected aggregates. Smaller q-values, like in the case of BNC, are not available at the setup because of insufficient incident neutron intensity.

The possibility to carry out SANS experiments at q-values of ~0.01 nm^{-1} is under discussion. It should be pointed out that this system is at the limit of possibilities of SANS diffractometers and requires time consuming experiments.

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Аксенов В.Л. и др. E14-2001-62

Структура фуллеренных агрегатов в растворе пиридин/вода
по данным малоуглового рассеяния нейтронов

Представлены результаты экспериментов по малоугловому рассеянию нейтронов на фуллеренах (C_{60}) в растворе пиридин/вода. Данные подтверждают выводы предыдущих исследований, в частности, по динамическому рассеянию света. В растворе формируются агрегаты с характерным радиусом около 20 нм. Вариация контраста с использованием различных комбинаций протонированных/дейтерированных компонентов (вода и пиридин) растворов указывает на малое содержание пиридина внутри агрегатов. Это свидетельствует о том, что агрегаты состоят из большого фуллеренного ядра, покрытого тонкой пиридиновой оболочкой.

Работа выполнена в Лаборатории нейтронной физики им. И.М.Франка ОИЯИ.

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Aksenov V.L. et al. E14-2001-62

Structure of Fullerene Aggregates in Pyridine/Water Solutions
by Small-Angle Neutron Scattering

Results of small-angle neutron scattering experiments on fullerenes (C_{60}) in pyridine/water solutions are reported. They confirm conclusions of the previous studies, in particular, dynamic light scattering experiments. Aggregates with characteristic radius of about 20 nm are formed in the solutions. The contrast variation using different combinations of protonated/deuterated components (water and pyridine) of the solutions points to the small pyridine content inside the aggregates. This fact testifies that the aggregates consist of a massive fullerene core covered by a thin pyridine shell.

The investigation has been performed at the Frank Laboratory of Neutron Physics, JINR.

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