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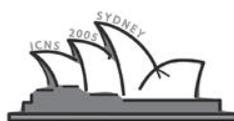
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Formation of fullerene clusters in the system C_{60} /NMP/water by SANS

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Abstract

Solutions of fullerenes in nitrogen-containing solvents constitute a specific class characterized by the formation of fullerene clusters. In the given work, we report the effect of cluster rearrangement in the system C_{60} /N-methylpyrrolidone (NMP) after addition of water (miscible with NMP) as observed by small-angle neutron scattering (SANS). The effect has a critical character and takes place if the water relative content is higher than 40%. Despite a small scattering signal, estimates of the mean scattering length density of the clusters by SANS contrast variation can be done.

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Keywords: Small-angle neutron scattering; Fullerene solutions; Clusters

1. Introduction

Recently, the clusterization of fullerene C_{60} in different nitrogen-containing solvents, as well as in their mixtures with water and other solvents has been reported [1–4]. The effect is connected with specific features of this class of solvents regarding the interaction with fullerenes. On the one hand, C_{60} may form charge-transfer complexes in these solvents, which facilitates its dissolution. On the other hand, comparatively strong polarity of the solvent molecules hinders the dissolution. A competition between the two factors together with a complex dissolution kinetics of C_{60} molecules result in the cluster formation. The clusterization of C_{60} can be a reason for solvatochromatic effects observed in these systems.

In the present work, we demonstrate that the cluster organization is sensitive to addition of water to such systems. This is done for the system C_{60} /N-methylpyrrolidone (NMP)/water. NMP is a comparatively good solvent for C_{60} (reported [5] solubility is 1240 μM) and is miscible with water. It can be used for fullerene transfer into aqueous media, which is of current interest with respect to

employing biological activity of fullerenes in medical applications. We use the small-angle neutron scattering (SANS) to detect changes in the cluster organization in the scale of 1–100 nm. In fact, for such systems SANS is a unique technique which allows to do this, as well as to estimate the inner structure of the clusters by means of the contrast variation.

2. Experimental

The solutions of fullerene C_{60} in NMP (up to 1000 μM) were prepared by gentle stirring during 4 days at room temperature. Ternary solutions C_{60} /NMP/ H_2O (up to 500 μM of C_{60}) were prepared by water dilution of C_{60} /NMP system. It is important to mention that the binary solvent NMP/ H_2O itself did not dissolve C_{60} . The UV–Vis spectra of the C_{60} /NMP solutions showed changes at 1 month after the preparation (slow solvatochromic effect) reflecting the formation of the clusters in the system. Dynamic light scattering (DLS) measurements for these solutions revealed clusters with a characteristic size of 500 nm. When water was added into the system, a small solvatochromic effect took place depending on the time interval between the preparation of the initial C_{60} /NMP solution and the addition of H_2O . The most pronounced

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changes in the UV–Vis spectrum took place if water was added to the fresh C_{60} /NMP solution (within 1 day after initial dissolution).

SANS experiments were performed at the small-angle diffractometers at the research reactors of the Budapest Neutron Center (Hungary) and the Joint Institute for Nuclear Research (Dubna, Russia) according to standard procedures. The observable SANS signal was registered in the q -interval of $0.1\text{--}1\text{ nm}^{-1}$ for the systems with different volume fractions of water from 0 to 0.7. The contrast variation based on mixtures of light and heavy water was made for the solution with relative water content of 0.5 so that the content of D_2O changed in the system from 0 to 0.5.

3. Results and discussion

Comparison of the SANS signals from systems C_{60} /NMP and C_{60} /NMP/ H_2O are presented in Fig. 1. One can see that the scattering from pure NMP solution is at the background level, while the addition of water results in its significant arise and reflects an effect of clusters within the size-interval of $10\text{--}100\text{ nm}$ corresponding to the covered q -range. A slight tendency toward less characteristic size of the clusters is observed in the DLS experiments, which is an indication that new clusters in the ternary system are a result of partial destruction of the large clusters in C_{60} /NMP on the addition of water. It should be pointed out that SANS experiments for these solutions are time consuming. It takes about 1 day of measurements for one sample at the involved setups to resolve a small coherent scattering against the high incoherent background from hydrogen in the solvents. Further estimations are made on the basis of shorter measurements, which allowed only the analysis of mean scattering intensity with a reasonable accuracy. Thus, the observed effect has a

critical character in respect to the water relative content and takes place when the latter approaches 40%, which is seen (Fig. 2) in the behavior of the mean scattering intensity referred to one concentration. The rate of the intensity change depends on the age of the initial C_{60} /NMP solutions, and it is less for older solutions.

The appearance of the SANS signal makes it possible to apply the contrast variation procedure for estimating the inner structure of the clusters. Again, to find out the match point of the mean cluster density we used the dependence of the mean scattering intensity on the D_2O content (Fig. 3). The precision of the determined match point is poor, 0.8 ± 0.3 ; however, its mean value corresponds well to the scattering length density $\rho \sim 5.6 \times 10^{10}\text{ cm}^{-2}$ of packed fullerene structures (crystals or highly packed amorphous clusters). From this, one can definitely conclude that there is no significant amount of binding of NMP in the structure of the fullerene clusters, which would correspond to the situation when clusters consist of solvated fullerene molecules. Similar conclusions were made for other fullerene dispersions in polar media [6–8].

The observed cluster rearrangement seems to be common for nitrogen-containing solvents which dissolve fullerenes [6,7], while its reason is unclear for the moment. We believe that it is connected with multiscaled cluster organization in the solutions, i.e. along with the first stage of the cluster formation, the secondary, ternary and so on take place as well. Water added to the system influences somewhat a last stage(s) and destroys it(them). A difference in the concomitant solvatochromic effect for different solvents indicates a variety in the cluster organizations in them. Also, it should be pointed out that the cluster destruction in the considered case is not a kinetic effect. If we dissolve the initial system with pure NMP in the same way as with H_2O , the effect does not take place.

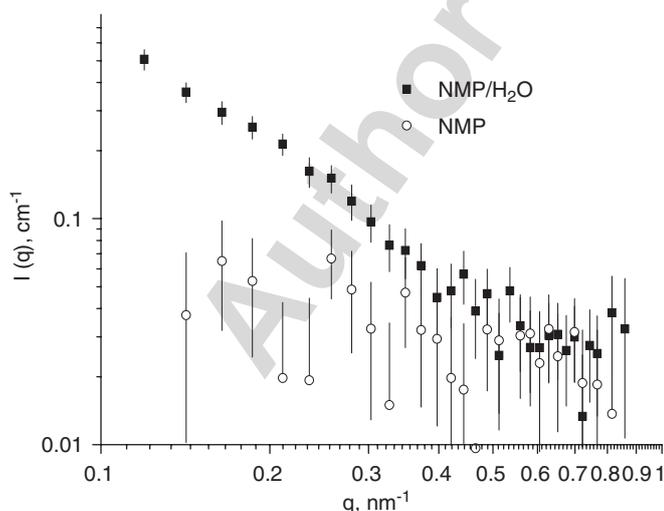


Fig. 1. SANS signals from systems C_{60} -NMP and C_{60} -NMP- H_2O with water content of 50 vol%. The concentration of C_{60} in both solutions is $500\text{ }\mu\text{M}$.

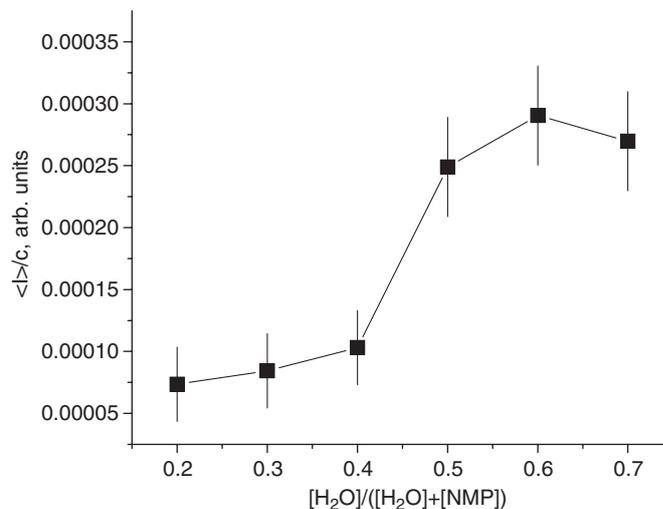


Fig. 2. Mean scattering intensity of the SANS signal (over q -interval of $0.14\text{--}0.44\text{ nm}^{-1}$) from system C_{60} -NMP- H_2O as a function of relative water content.

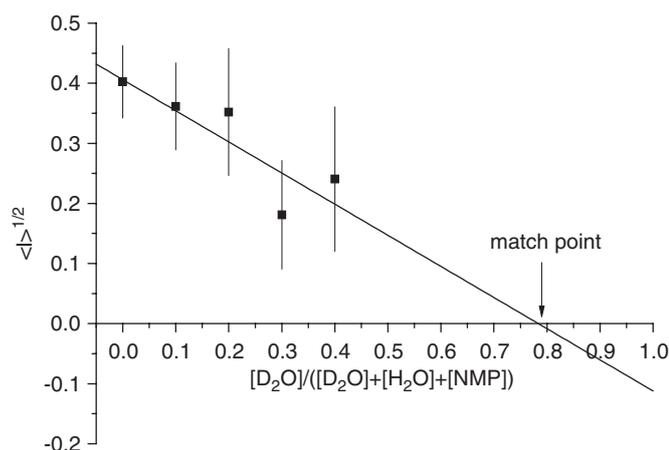


Fig. 3. Contrast variation in the system C₆₀–NMP–H₂O/D₂O. The mean scattering intensity is determined for q -interval of 0.14–0.44 nm⁻¹.

4. Conclusions

Our SANS study shows that large stable clusters (size >100 nm) in the C₆₀–NMP solution partially dissociate into smaller ones (size <100 nm) on addition of water. The effect has a sharp character when the water content in the system approaches 40 vol%. The contrast variation indicates that these clusters are close to fullerene crystals or highly packed amorphous structures of fullerene molecules. Previously, similar conclusions were made [6,7] for the system with other nitrogen-containing solvent, pyridine, where the solvatochromic effects are significantly higher

than in the present system. The systems studied are in many respects similar to colloidal solutions of fullerene C₆₀ in water [8]. This makes the study of fullerene solutions in nitrogen-containing solvents very important for understanding of the C₆₀–water interaction and development of new ways to transfer fullerenes into aqueous media.

Acknowledgments

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