https://doi.org/10.15407/ujpe63.2.116

L.A. BULAVIN,[1,2] T.V. NAGORNA,[1,3] O.A. KYZYMA,[1,3] D. CHUDOBA,[3,4] O.I. IVANKOV,[2] A.V. NAGORNYI,[1,3] M.V. AVDEEV[3]

[1] Taras Shevchenko National University of Kyiv
(2, Academician Glushkov Ave., Kyiv 03022, Ukraine)

[2] Institute for Safety Problems of Nuclear Power Plants, Nat. Acad. of Sci. of Ukraine
(12, Lysogirska Str., Bld. 106, Kyiv 03028, Ukraine)

[3] Joint Institute for Nuclear Research
(6, Joliot-Curie Str., Dubna 141980, Russian Federation; e-mail: tanya@nf.jinr.ru)

[4] Uniwersytet im. Adama Mickiewicza w Poznaniu
(ul. Wieniawskiego 1, Poznań 61-712, Poland)

FULLERENE CLUSTERING IN C_{70}/N-METHYl-2-PYRROLIDONE/TOLUENE LIQUID SYSTEM

The structural behavior of the liquid system based on a C_{70} in an N-methyl-2-pyrrolidone–toluene mixture has been analyzed, by using the small-angle neutron scattering method. The experimental results testify to the selective solvation in the system. The corresponding mechanisms have been discussed.

Keywords: C_{70} fullerene clustering, small-angle neutron scattering.

1. Introduction

Since fullerenes, a new allotropic form of carbon, have been discovered, the possibilities of their application in various domains, including electronics, optics, cosmetology, and pharmaceutics, have been actively studied [1–3]. Such attention is invoked by a number of interesting properties of fullerenes. In particular, this is their solubility in aromatic solvents [4–7], which considerably extends the areas of their possible application.

The interest in the research of mixtures with fullerenes is associated, first of all, with technological conditions required for the fabrication and purification of fullerenes, as well as with the synthesis of aqueous systems for their biological application [8, 9]. Despite that it is the transfer of C_{60}/C_{70} from an organic solvent to water that is most often used for the preparation of aqueous mixtures with fullerenes, the processes running in a liquid system containing both polar and nonpolar liquids have not been studied at length. For instance, it was demonstrated recently that the structure and properties of an aqueous system obtained with the use of a certain synthesis method depend on the choice of a primary organic solvent [10]. On the other hand, the observed clustering in nonpolar solvents [11, 12] that are characterized by a high fullerene solubility [13] puts additional questions concerning the origin of fullerene clustering in various liquid systems.

Earlier, the fullerene clustering was assumed to take place at a definite solvent polarity. In particular, specific values of the solvent dielectric constant were determined [14, 15] and specified [16], at which the fullerene clustering begins: $\varepsilon = 13$ [14] and $\varepsilon = 19 \div 23$ [16] for C_{60}, and $\varepsilon = 27 \div 31$ for C_{70} [15]. However, in view of the results of recent works dealing with the fullerene clustering in nonpolar solvents, a conclusion can be drawn that this process has a more complicated character.

In this work, using the method of small-angle neutron scattering (SANS), the clustering of fullerene C_{70} in its mixtures with polar and nonpolar solvents has been studied. Toluene ($\varepsilon = 2.37$) and N-methyl-2-pyrrolidone ($\varepsilon = 32$), which are characterized by absolute solubility, were selected as solvents. Researches of the fullerene clustering in mixtures with the polar solvent N-methyl-2-pyrrolidone (NMP) were carried out earlier [6, 17–25]. The results of researches demonstrated that, in time, fullerenes transit from the monomer state to aggregates [26, 27].

Besides a high solubility of fullerenes in NMP, this solvent is considered to be absolutely soluble in water, which is important for the preparation of fullerene mixtures with both water and NMP [28]. When fullerene is transferred from NMP to water, the formation of stable clusters is most likely achieved due to the formation of donor-acceptor complexes containing fullerene C_{60} and NMP molecules [29]. With this point in view, the processes of C_{70} clustering were studied both when NMP was added to the C_{70}/toluene mixture and when the C_{70}/NMP mixture was diluted with toluene.

2. Materials and Methods

Specimens were prepared, by using the following materials: fullerene C_{70} (*Fullerene Technologies*, a purity higher than 99.5%), toluene (*Merck*, a purity higher than 99.5%), and N-methyl-2-pyrrolidone (*Merck*, a purity higher than 99.5%). The initial mixtures C_{70}/toluene (with a concentration of 0.73 mg/ml) and C_{70}/NMP (with a concentration of 0.61 mg/ml) were prepared, by mixing them for 15 min at room temperature making use of a magnetic stirrer. In a week after the preparation of a corresponding mixture, the other liquid was added, and three-component liquid systems C_{70}/toluene/NMP and C_{70}/NMP/toluene were obtained. For our research, specimens with the following volume fractions of the third component (NMP or toluene, respectively) were fabricated: 0, 20, 30, 40, 50, 60, and 80 vol.%.

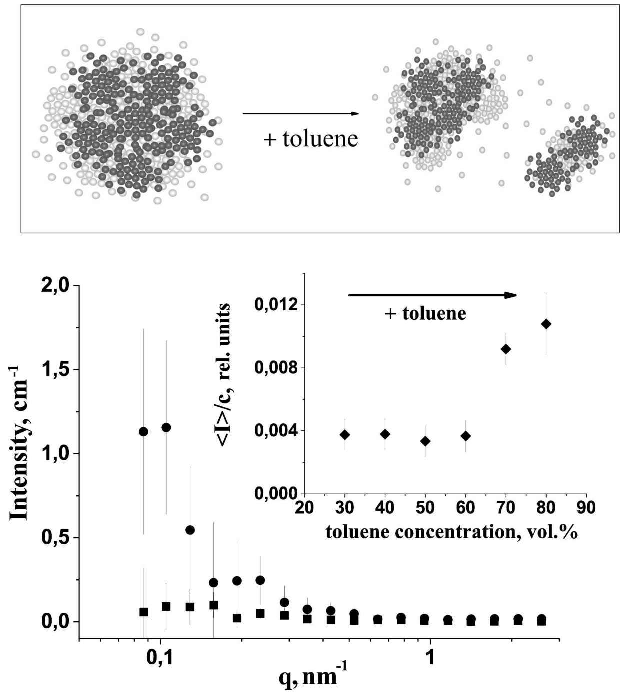

Fig. 1. Experimental small-angle neutron scattering (SANS) curves for the C_{70}/N-methyl-2-pyrrolidone (NMP) mixture (squares) and with the addition of toluene to 80 vol.% (circles). The spectra are normalized by the fullerene concentration. The dependence of the integral scattering intensity on the second solvent (toluene) content in the interval $q = 0.1 \div 0.5$ nm^{-1} is shown in the inset

SANS experiments were carried out for the liquid systems C_{70}/toluene and C_{70}/NMP in a week after their preparation. The other solvent (NMP or toluene, respectively) was added to the initial liquid mixture with fullerenes immediately before the neutron experiment.

SANS measurements were performed on a YuMO installation of the IBR-2 reactor at the Joint Institute for Nuclear Research (Dubna, Russia). The dependences of the differential scattering cross-section per specimen volume unit (hereafter, the scattering intensity $I(q)$) were measured, by using the neutron time-of-flight method in the interval of transferred momentum vector magnitudes $q = 0.05 \div 5$ nm^{-1}. Specimens 500 μl in volume were poured into 1-mm quartz cuvettes (*Hellma Analytics*), which were held at a temperature of 20 °C. The solvents and their mixtures without fullerene, the so-called buffer specimens, were used as reference ones. A standard vanadium specimen was used to calibrate the intensity of

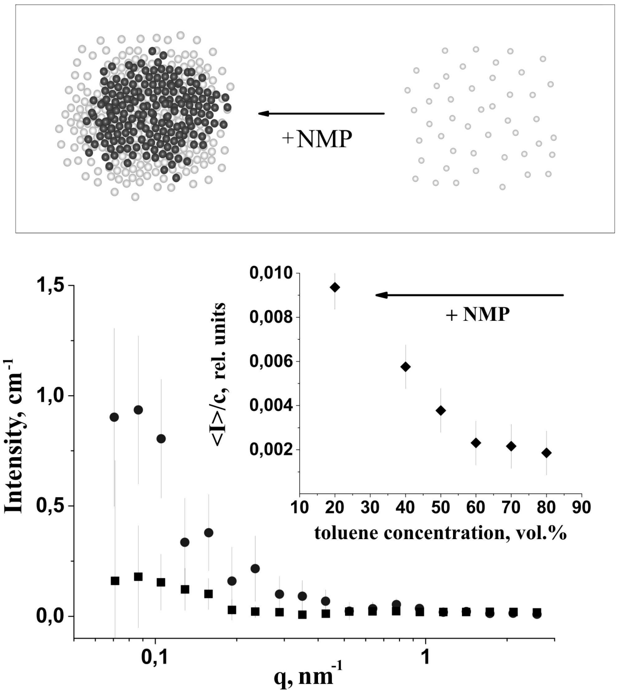

Fig. 2. Experimental SANS curves for the C_{70}/toluene mixture (squares) and with the addition of NMP to 80 vol.% (circles). The spectra are normalized by the fullerene concentration. The dependence of the integral scattering intensity on the second solvent (NMP) content in the interval $q = 0.1 \div 0.5\ \text{nm}^{-1}$ is shown in the inset

neutron scattering [30, 31]. The data obtained were processed, by using the SAS software in the smoothing mode [32].

3. Results and Their Discussion

The SANS spectra obtained for the systems C_{70}/NMP and C_{70}/NMP/toluene with a toluene concentration of 80 vol.% are depicted in Fig. 1. It is evident that the spectra are different at small q's: the triple mixture is characterized by a clear signal in the Guinier region (circles), whereas the SANS curve for the C_{70}/NMP mixture (squares) remains at the background level within the whole interval of the variable q. The experimental SANS curves exhibited in Fig. 1 can be explained as follows. In the C_{70}/NMP mixture, there emerge clusters of fullerene C_{70} with dimensions of above 100 nm [33], which goes beyond the detection limits of the YuMO installation. However, if the third component, toluene, is added, the fullerene clusters in the C_{70}/NMP mixture are reorganized. Namely, large clusters become partially destroyed (see the illustration in Fig. 1). The appearance of a neutron signal at the beginning of the spectrum reflects this fact.

Hence, the observed SANS phenomenon can be interpreted as the emergence of a significant number of fullerene clusters with dimensions less than $D = 2\pi/q_{\min} \approx 70$ nm in the C_{70}/NMP solution. The cluster reorganization is a result of the increase in the nonpolar component fraction – namely, toluene – which has a higher solubility (1.4 mg/ml [**?**]) in comparison with that of polar NMP. In spite of a poor statistics provided by the neutron experiment, we analyzed the integral scattering intensity, which can be a measure for the concentration of those clusters in the system, whose dimensions correspond to the installation sensitivity interval. Basing on a number of SANS spectra measured for the C_{70}/NMP/toluene system, the dependence of the integral SANS intensity on the toluene volume fraction was plotted. This dependence is shown in the insert in Fig. 1. As one can see, it drastically changes, when the concentration of toluene in the system exceeds 60 vol.%.

The SANS spectra registered for the system C_{70}/toluene with the addition of the polar NMP solvent are shown in Fig. 2. The scattering in the C_{70}/toluene mixture remains within the background level. At the same time, the addition of the polar NMP component gives rise to the appearance of a pronounced neutron signal: the intensity at the initial section of the SANS spectrum increases. This effect takes place because the detection of C_{70} monomers in toluene is a difficult task, whereas the addition of NMP stimulates clustering of fullerenes, which results in the neutron scattering growth. As follows from the analysis of the dependence shown in the inset in Fig. 2, when the volume fraction of NMP increases from 40% to 80% and, accordingly, the volume fraction of toluene decreases from 60% to 20% (the direction is indicated by an arrow in Fig. 2), the integral intensity of neutron scattering increases monotonically. This behavior testifies to the formation of fullerene clusters, when the toluene content decreases and the solution polarity increases, as is illustrated Fig. 2.

Hence, the reorganization of C_{70} clusters in the C_{70}/NMP/toluene mixture was observed for the toluene concentrations higher than 60 vol.%. Earlier, a critical destruction of fullerene C_{60} clusters was revealed in the C_{60}/NMP/toluene [35] and C_{60}/NMP/water [36, 37] mixtures. However, the destruction of fullerene C_{60} clusters was observed, when the concentration of the third component (water or toluene) in the mixture exceeded 40 vol.% [35].

It should be noted that the addition of the polar NMP solvent to the C_{70}/toluene mixture did not result in a smooth growth of fullerene clusters and, accordingly, was not reflected in the SANS spectra. In particular, a critical character of the fullerene clustering effect, when the polar component concentration reaches or exceeds 40 vol.% ($\varepsilon = 6.71$), testifies to a specific solvation in the liquid system.

4. Conclusions

To summarize, the effect of selective molecular solvation for either of the examined solvents near C_{70} molecules is observed. The corresponding equisolvation point corresponds to a solution with a toluene concentration of 60 vol.%. The composition of a solvate shell has equal content fractions of solvents in this case, but differs from the composition of solvents in the liquid system bulk. In effect, we observe a selective accumulation of NMP molecules in the nearest solvate shell of C_{70}. With regard for a higher polarity of NMR in comparison with that of toluene, a conclusion can be made that this solvation is initiated, first of all, by the formation of C_{70}–NMP complexes [29], in which fullerene plays the role of an electron acceptor for electronegative atoms entering the NMP composition. Earlier, the formation of such complexes was suggested, when studying the absorption spectra of the C_{60}/NMP mixtures and their solutions [38,39].

1. L. Wang. Solvated fullerenes, a new class of carbon materials suitable for high-pressure studies: A review. *J. Phys. Chem. Solids* **84**, 85 (2015).
2. M. Xing, R. Wang, J. Yu. Application of fullerene C_{60} nano-oil for performance enhancement of domestic refrigerator compressors. *Int. J. Refrig.* **40**, 398 (2014).
3. S. Afreen, K. Muthoosamy, S. Manickam *et al.* Functionalized fullerene (C_{60}) as a potential nanomediator in the fabrication of highly sensitive biosensors. *Biosens. Bioelectr.* **63**, 354 (2015).
4. A.V. Eletskii, B.M. Smirnov. Fullerenes and carbon structure. *Usp. Fiz. Nauk* **165**, 977 (1995) (in Russian).
5. Y. Marcus. Solubilities of buckminsterfullerene and sulfur hexafluoride in various solvents. *J. Phys. Chem.* **101**, 942 (1997).
6. Y. Marcus, A.L. Smith, M.V. Korobov *et al.* Solubility of C_{60} fullerene. *J. Phys. Chem. B* **105**, 13 (2001).
7. A.N. Kinchin, A.M. Kolker, N.I Islamova. Correlation between the thermodynamic parameters of fullerene C_{60} solution and the properties of non-aqueous solvents. *Zh. Fiz. Khim.* **76**, 1772 (2002) (in Russian).
8. J. Labille, J. Brant, F. Villieras *et al.* Affinity of C_{60} fullerenes with water. *Fulleren. Nanotub. Carbon Nanostruct.* **14**, 307 (2006).
9. I.E. Serdyuk, I.V. Belochkina, A.P. Kryshtal, A.D. Roshal, I.M. Neklyudov, B.V. Borshch, V.N. Voevodin, V.I. Tkachenko, B.P. Sandomirskii. Production and biological activity of aqueous colloidal solutions of C_{60} and C_{70} fullerene mixtures. *Biotekhnologiya* **4**, 64 (2011) (in Russian).
10. S. Yang, X. Mulet, T. Gengenbach *et al.* Limitations with solvent exchange methods for synthesis of colloidal fullerenes. *Colloid. Surface. A* **514**, 21 (2017).
11. R.-H. Guo, C.-C. Hua, P.-C. Lin, T.-Y. Wang, S.-A. Chen. Mesoscale aggregation properties of C_{60} in toluene and chlorobenzene, *Soft Matter* **12**, 6300 (2016).
12. U. Makhmanov, O. Ismailova, A. Kokhkharov *et al.* Features of self-aggregation of C_{60} molecules in toluene prepared by different methods. *Phys. Lett. A* **380**, 2081 (2016).
13. A.V. Eletskii, B.M. Smirnov. Fullerenes in solutions, *Usp. Fiz. Nauk* **168**, 1195 (1995).
14. S. Nath, H. Pal, A. Sapre. Effect of solvent polarity on the aggregation of C_{60}. *Chem. Phys. Lett.* **327**, 143 (2000).
15. S. Nath, H. Pal, A. Sapre. Effect of solvent polarity on the aggregation of fullerenes: a comparison between C_{60} and C_{70}. *Chem. Phys. Lett.* **360**, 422 (2002).
16. N.O. Mchedlov-Petrossyan, N.N. Kamneva, Y.T.M. Al-Shuuchi, A.I. Marynin, S.V. Shekhovtsov. The peculiar behavior of fullerene C_{60} in mixtures of 'good' and polar solvents: Colloidal particles in the toluene–methanol mixtures and some other systems. *Colloid. Surface. A* **509** 631 (2016).
17. M. Alfé, B. Apicella, R. Barbella, A. Bruno, A. Ciajolo. Aggregation and interactions of C_{60} and C_{70} fullerenes in neat N-methylpyrrolidinone and in N-methylpyrrolidinone/toluene mixtures. *Chem. Phys. Lett.* **405**, 193 (2005).
18. M. Alfé, R. Barbella, A. Bruno, P. Minutolo, A. Ciajolo. Solution behaviour of C_{60} fullerene in N-methylpyrrolidinone/toluene mixtures. *Carbon* **43**, 665 (2005).
19. V.L. Aksenov, T.V. Tropin, O.A. Kyzyma, M.V. Avdeev, M.V. Korobov, L. Roshta. To fullerene C_{60} clustering in nitrogen-containing solvents. *Fiz. Tverd. Tela* **52**, 992 (2010) (in Russian).
20. O.A. Kyzyma, M.V. Korobov, M.V. Avdeev, V.M. Garamus, V.I. Petrenko, V.L. Aksenov, L.A. Bulavin. Solvatochromism and fullerene cluster formation in C_{60}/N-methyl-2-pyrrolidone. *Fulleren. Nanotub. Carbon Nanostruct.***18**, 458 (2010).
21. T.V. Nagorna, O.A. Kyzyma, D.Chudoba, A.V. Nagornyi. Temporal solvatochromic effect in ternary C_{70}/toluene/N-

methyl-pyrrolidine-2-one solution. *J. Mol. Liq.* **235**, 111 (2017).

22. M.V. Avdeev, V.L. Aksenov, T.V. Tropin. Models of fullerene clustering in solutions. *Zh. Fiz. Khim.* **84**, 1405 (2010) (in Russian).
23. N.O. Mchedlov-Petrossyan. Fullerenes in molecular liquids. Solutions in "good" solvents: Another view. *J. Mol. Liq.* **161**, 1 (2011).
24. C.M. Sayes, J.D. Fortner, W. Guo, D. Lyon, A.M. Boyd, K.D. Ausman, Y.J. Tao, B. Sitharaman, L.J. Wilson, J.B. Hughes, J.L. West, V.L. Colvin. The differential cytotoxicity of water-soluble fullerenes. *Nano Lett.* **4**, 1881 (2004).
25. O.A. Kyzyma, A.V. Tomchuk, M.V. Avdeev, T.V. Tropin, V.L. Aksenov, M.V. Korobov. Structural researches of carbonic fluid nanosystems. *Ukr. J. Phys.* **60**, 835 (2015).
26. T.V. Tropin, M.V. Avdeev, O.A. Kyzyma, V.L. Aksenov. Nucleation theory models for describing kinetics of cluster growth in C_{60}/NMP solutions. *Phys. Status Solidi B* **247**, 3022 (2010).
27. T.V. Tropin, N. Jargalan, M.V. Avdeev, O.A. Kyzyma, R.A. Eremin, D. Sangaa, V.L. Aksenov. Kinetics of cluster growth in polar solutions of fullerene: Experimental and theoretical study of C_{60}/NMP solution. *J. Mol. Liq.* **175,** 4 (2012).
28. S. Andreev, D. Purgina, E. Bashkatova *et al.* Study of fullerene aqueous dispersion prepared by novel dialysis method: simple way to fullerene aqueous solution. *Fulleren. Nanotub. Carbon Nanostruct.* **23**, 7 (2015).
29. N.P. Yevlampieva, Yu.F. Biryulin, E.Yu. Melenevskaja, V.N. Zgonnik, E.I. Rjumtsev. Aggregation of fullerene C_{60} in N-methylpyrrolidone. *Colloid. Surface. A* **209**, 167 (2002).
30. A.I. Kuklin, D.V. Soloviov, A.V. Rogachev *et al.* New opportunities provided by modernized small-angle neutron scattering two-detector system instrument (YuMO). *J. Phys. Conf. Ser.* **291**, 1 (2011).
31. Yu.I. Prylutskyy, V.I. Petrenko, O.I. Ivankov, O.A. Kyzyma, L.A. Bulavin, O.O. Litsis, M.P. Evstigneev, V.V. Cherepanov, A.G. Naumovets, U. Ritter. On the origin of C_{60} fullerene solubility in aqueous solution. *Langmuir* **30**, 3967 (2014).
32. A.G. Soloviev, T.M. Solovieva, A.V. Stadnik *et al.* The upgrade of package for preliminary treatment of small-angle scattering spectra. *JINR Commun.* **10**, 2003 (2003).
33. A.A. Kaznacheevskaya, O.A. Kizima, L.A. Bulavin, A.V. Tomchuk,V.M. Garamus, M.V. Avdeev. Reorganization of the cluster state in a C_{60}/N-methylpyrrolidone/water solution: Comparative characteristics of dynamic light scattering and small-angle neutron scattering data. *J. Surf. Invest. X-ray Synchr. Neutr. Techn.* **7**, 1133 (2013).
34. . Sivaraman, R. Dhamodaran, I. Kaliappan *et al.* Solubility of C_{70} in organic solvents. *Fullerene Sci. Technol.* **2** (3), 233 (1994).
35. T.V. Tropin, T.O. Kyrey, O.A. Kyzyma, A.V. Feoktistov, M.V. Avdeev, L.A. Bulavin, L. Rosta, V.L. Aksenov. Experimental investigation of C_{60}/NMP/toluene solutions by UV-Vis spectroscopy and small-angle neutron scattering, *J. Surf. Invest. X-ray, Synchrotron Neutron Techn.* **7**, 1 (2013).
36. O.A. Kyzyma, M.V. Korobov, M.V. Avdeev, V.M. Garamus, S.V. Snegir, V.I. Petrenko, V.L. Aksenov, L.A. Bulavin. Aggregate development in C_{60}/N-metyl-2-pyrrolidone solution and its mixture with water as revealed by extraction and mass spectroscopy. *Chem. Phys. Lett.* **493**, 103 (2010).
37. O.A. Kyzyma, L.A. Bulavin, V.L. Aksenov, M.V. Avdeev, T.V. Tropin, M.V. Korobov, S.V. Snegir, L. Rosta. Aggregation in C_{60}/NMP, C_{60}/NMP/water and C_{60}/NMP/toluene mixtures. *Fulleren. Nanotub. Carbon Nanostruct.* **16**, 610 (2008).
38. T.O. Kyrey, O.A. Kyzyma, M.V. Avdeev, T.V. Tropin, M.V. Korobov, V.L. Aksenov, L.A. Bulavin. Absorption characteristics of fullerene C_{60} in N-methyl-2-pirrolidone/toluene mixture. *Fulleren. Nanotub. Carbon Nanostruct.* **20**, 341 (2012).
39. O.A. Kyzyma, T.O. Kyrey, M.V. Avdeev, M.V. Korobov, L.A. Bulavin, V.L. Aksenov. Non-reversible solvatochromism in N-methyl-2-pyrrolidone/toluene mixed solutions of fullerene C_{60}. *Chem. Phys. Lett.* **556**, 178 (2013).

Received 23.06.17.
Translated from Ukrainian by O.I. Voitenko

Л.А. Булавін, Т.В. Нагорна, О.А. Кизима,
Д. Худоба, О.І. Іваньков, А.В. Нагорний, М.В. Авдеєв

КЛАСТЕРОУТВОРЕННЯ ФУЛЕРЕНІВ У РІДИННІЙ СИСТЕМІ C_{70}–N-МЕТИЛ-2-ПІРОЛІДОН–ТОЛУОЛ

Р е з ю м е

У роботі методом малокутового розсіяння нейтронів проаналізовано поведінку рідинної системи C_{70}–N-метил-2-піролідон–толуол. Результати експериментів вказують на наявність селективної сольватації системи, причини якої обговорюються.