

Communication

^{14}N NMR Spectroscopy Study of Binding Interaction between Sodium Azide and Hydrated Fullerene

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Abstract: Our study is the first attempt to study the interaction between NaN_3 and hydrated fullerenes C_{60} by means of a non-chemical reaction-based approach. The aim is to study deviations of signals obtained by ^{14}N NMR spectroscopy to detect the binding interaction between sodium azide and hydrated fullerene. We considered ^{14}N NMR spectroscopy as one of the most suitable methods for the characterization of azides to show resonance signals corresponding to the three non-equivalent nitrogen atoms. The results demonstrate that there are changes in the chemical shift positions and line-broadening, which are related to the different molar ratios of $\text{NaN}_3:\text{C}_{60}$ in the samples.

Keywords: sodium azide; fullerene; ^{14}N NMR spectroscopy; nanofiltration

1. Introduction

The presence of pharmaceutical active compounds (PhACs) in surface, drinking, and wastewaters is an emerging issue in environmental science [1–9]. Low levels of many pharmaceutical active compounds are detected in the aquatic environment as a result of pharmaco-chemical industrial waste spill-off in draining water. It may be necessary to demonstrate that these impurities are sufficiently removed to levels below an appropriate safety threshold.

Sodium azide is an example of an azide for which the environmental exposure limits have been reasonably well characterized. The Organization for Economic Co-operation and Development (OCDE) [10] has included sodium azide in the list of 5235 High Production Volume Chemicals (HPV) with a production or import greater than 1000 tons per year [10]. Environmentalists and atmospheric scientists are concerned about the safety of the use of sodium azide. Despite the widespread opinion of proponents of sodium azide use in water and soil, who argue that this chemical undergoes rapid hydrolysis and degradation [11,12], their opponents [13] claim that this is not exactly what can be anticipated, since they have discovered water and soil samples containing residual amounts of sodium azide.

The detection and inactivation of sodium azide in the environment is a global issue, due to its widespread use in many spheres of human activity, including the pharmaco-chemical industry in the synthesis of pharmaceuticals; its direct use in the agricultural sphere in herbicides, pesticides and insecticides; its use as a wine fermentation inhibitor; and its use in the automotive industry, in the content of airbag detonators and bactericidal agents for the inhibition of germ growth. In the manufacturing of pharmaceutical drug substances, azides are used in their synthesis or they are generated as an intermediate substance. Sodium azide (NaN_3) is widely used as starting molecule in

the synthesis of Sartans, a group of drugs that have been used for the treatment of hypertension since the 1990s [14]. Some of these products have reached a market volume of several 100 t/a with an upward trend and are therefore considered as blockbusters. Besides Sartans, it is used in the synthesis other pharmaceuticals such as Alfentanil (analgesic), Azosemid (diuretic), Broperamol (anti-inflammatory), and others.

Sodium azide (NaN_3) has an inhibitory effect on heme-containing mitochondrial respiratory chain enzyme Cytochrome C Oxidase, which is the cause of central nervous system (CNS) anoxia and hypoxia in the case of acute intoxication, while it can cause dementia in the case of a long-term, chronic exposure to lower doses. No antidote against NaN_3 is known to exist. In the case of chronic intoxication, prevention is possible by the administration of antioxidants to industrial workers. For the prevention of these impacts, it is important to decrease the risk of exposure to sodium azide in the occupation workplace atmosphere as well as in the environment.

There are required regulations for the analysis of pharmaceutical wastewater treatment and removal using membrane bioreactors (MBR). The water treatment can be conducted by removing dissolved materials and ions using membrane separation technology with ultra- and nanofiltration (NF) and reverse osmosis (RO) membranes [15]. Many studies considering the removal of toxic anions from natural waters and purified wastewaters showed promising results [16].

One of the most important issues is the control of runoff waters and the installation of adequate membrane filtration barriers. For industrial wastewater as well municipal and hospital dialysis centers, water treatment systems use modern membrane filtration technologies.

Physicochemical modifications of membrane materials have been attempted to improve the performance of membrane processes for a long time. Numerous studies dealing with the surface modification of membranes have achieved, by coating or grafting, a functional group on the prepared membrane surface [17].

In addition to the conventional ways of surface modification, researchers are focusing on the application of nanomaterials to modify membrane properties by incorporating recent developments of nanotechnologies. Surface modification of NF membranes is well reviewed and documented by Liu et al. (2011) [18]. Among others, fullerene (C_{60}) is the potential candidate expected to show an improved performance when used to modify membrane properties [19–21]. In 2009, Chae and coworkers developed a new technology of membrane dip-coating by hydrated fullerene for the improvement of membrane filtration properties [22]. Chae et al. (2009) also examined the modification of ceramic microfiltration membranes coated by fullerene solution dip-coat-evaporation procedure (Figure 1) [23]. The dip-coating procedure consisted of an initial immersion of the membrane into a solution for 2 s, drip-draining of the excess solvent, and finally solvent evaporation under vacuum for several days. The surface concentration of C_{60} on the membranes was varied by repeating the dip-coating procedure anywhere from one to nine times. The final concentration of C_{60} on the membrane was determined by measuring the change in membrane weight. The surface morphology of the membrane coated with various amounts of C_{60} was investigated using a scanning probe microscope (SPM). The C_{60} nanoparticles used in this study were not chemically bound to the membrane surface.

Besides fullerene-coated NF systems, carbon filters containing fullerenes are also used for water treatment. To achieve better effluent water quality, tertiary treatment with activated carbon adsorption is used [24]. Activated carbon filters, which may contain fullerenes, are capable of an extremely effective mechanical filtration effect [25–28].

To analyze the risk of pharmaceuticals in the environment, the proposed and validated methodology of NMR spectroscopy will support the evaluation of the eco-toxicological hazards of PhACs during this early development process.

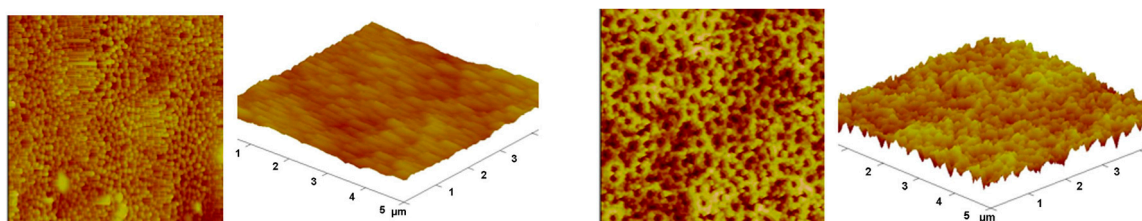


Figure 1. Surface morphology of ceramic membranes: (left) 200-nm anodisc with 0.030 mg of C60 per cm^{-2} and (right) 200-nm thick anodisc with 0.058 mg of C60 per cm^{-2} [23].

2. Materials and Methods

We aim to study deviations of signals obtained by ^{14}N NMR spectroscopy for the detection of the binding interaction between sodium azide and hydrated fullerene.

We studied binding properties between sodium azide and hydrated fullerene, without adding any catalyst, heating, or microwave irradiation, under conventional conditions to see if any interaction may occur to recommend in water filtration and pharmaceutical waste-water treatment applications, e.g., in different phases of filtration, such as in membranes and carbon filters enriched by fullerenes.

The experimental part of this project was performed in the Magnetic Resonance Unit at the Center of Technology Innovation and Transfer (CACTUS) of the University of Santiago de Compostela. Experiments were conducted during 2012–2014 and obtained results analyzed.

University of Santiago de Compostela (USC) is equipped with NMR spectroscopy and propriety technology of MESTRE Labs, which is the software used worldwide.

The Magnetic Resonance Unit at the University of Santiago de Compostela provides the optimum research instrumentation required for this part of the project. The NMR facility provides three state-of-the-art high magnetic field NMR spectrometers of 500 and 750 MHz.

2.1. Experimental

C60HyFn production, Characterization and Preparation of C60FWS

For C60FWS preparation (C60HyFn water solution), C60 fullerene samples with a purity of more than 99.5% (MER Corporation, Tuscon, AZ, USA) was used. C60FWS was produced without using of any solubilizers or chemical modifications [29].

C60HyFn concentration of 8.88×10^{-4} M was used as a stock solution for preparing C60FWS prior the experiment. This method is based on transferring fullerene from organic solution into the aqueous phase with the help of ultrasonic treatment. To obtain C60FWS, C60 of a concentration up to 5.5×10^{-3} M (~ 4 mg/mL) was used.

2.2. Titration

We added hydrated fullerene 50 mM solution (144 mg/L) (IPACOM, Kharkov, Ukraine) to sodium azide water solution with titration.

In our study, we performed a series of experiments with different concentrations of sodium azide with molar concentrations below and equivalent to 1 M, as well as higher molar concentrations to a maximum of 10 M.

In the first set of experiments, we used the standard addition method of titration. We performed adding titration technique on fullerene/water solutions of different concentrations. The standard ratios of NaN_3 :C60 used were 10:1; 1.36:1; 0.88:1; 0.38:1 and 100:1 (Figures 2–4).

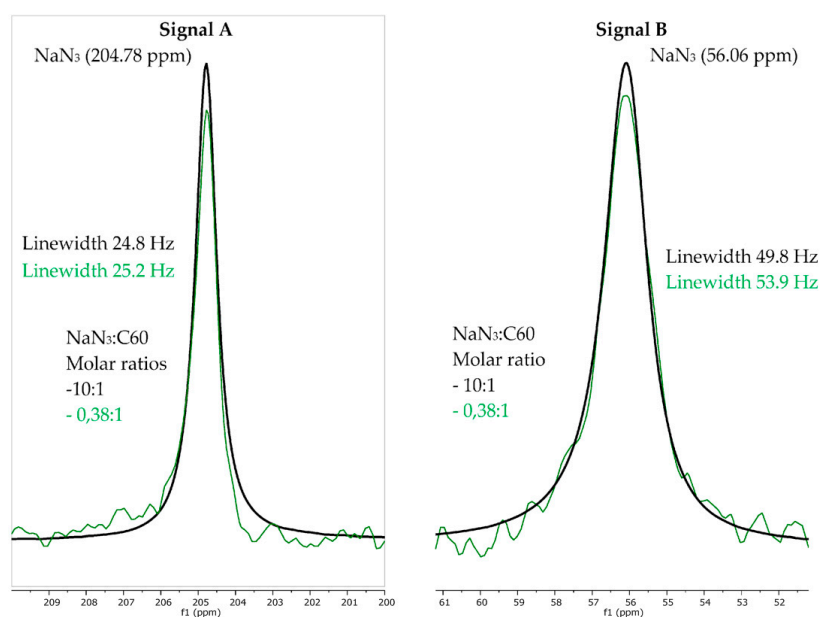


Figure 2. At low molar ratio NaN₃:C60 ($\leq 10:1$), ¹⁴N chemical shifts are observed for two peaks of NaN₃ (Signals A and B).

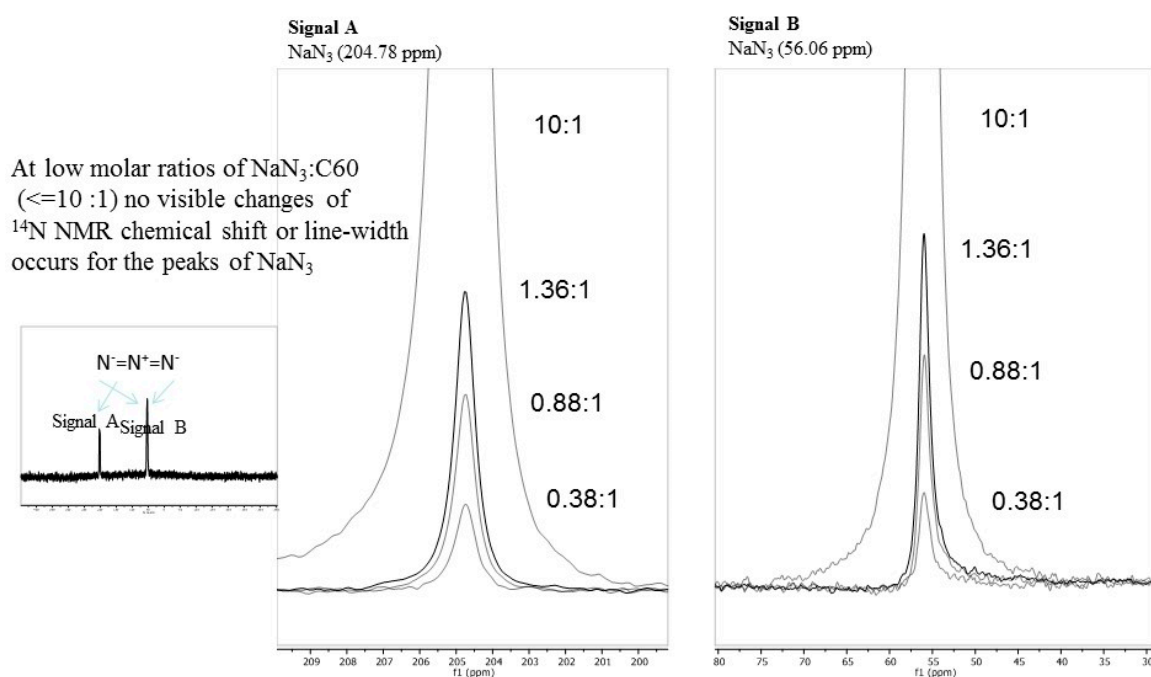


Figure 3. ¹⁴N NMR superimposition of four different spectra at low molar ratios of NaN₃:C60 ($\leq 10:1$).

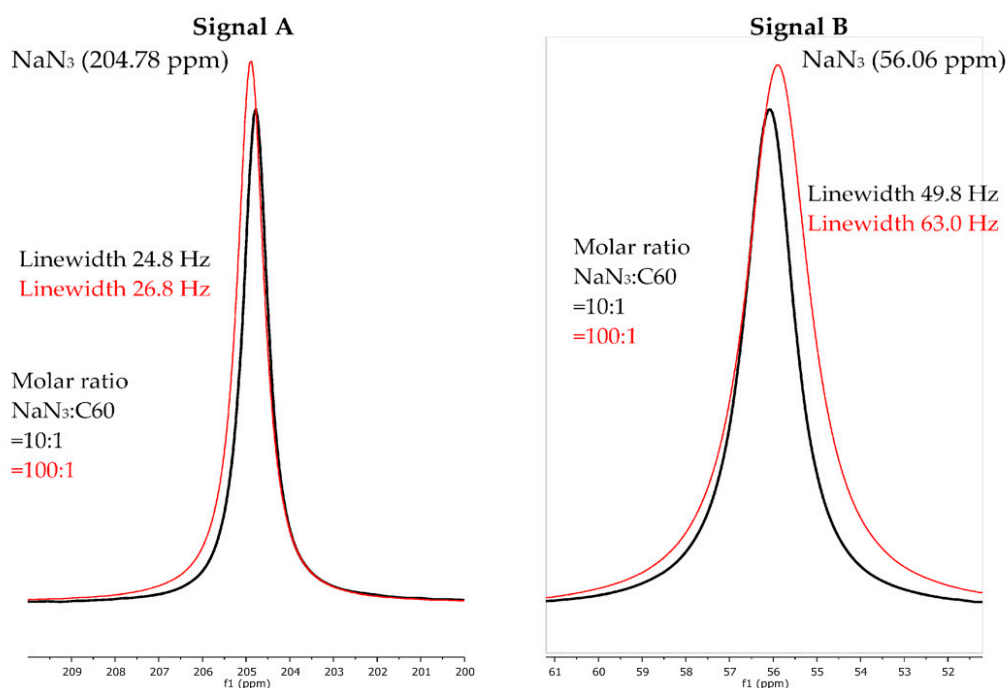


Figure 4. Superimposition of two spectra at a high ratio of $\text{NaN}_3:\text{C}_{60}$ ($>10:1$), specifically 100:1. There are some subtle changes in the ^{14}N chemical shift and line-width of both NaN_3 peaks (Signals **A** and **B**).

Thus, ratios of $\text{NaN}_3:\text{C}_{60}$ were equivalent to or less than 10:1 in the first set of experiments. In the second set, we used the highest concentration of 10 M sodium azide with the maximum ratio of $\text{NaN}_3:\text{C}_{60}$, which was equal to 100:1.

3. Results

Our study is the first attempt to study the interaction between NaN_3 and C_{60} hydrated fullerenes by means of a non-chemical reaction-based approach. We considered ^{14}N NMR spectroscopy as one of the most suitable methods for the characterization of azides to show resonance signals corresponding to the three non-equivalent nitrogen atoms.

We performed ^{14}N NMR spectroscopy of pure sodium azide water solution (Sigma Aldrich, St. Louis, MO, USA) and obtained satisfactory results, with the visualization of two peaks corresponding to three atoms of nitrogen with chemical shifts corresponding to 204.78 and 56.06 ppm [30].

A 1D ^{14}N NMR spectrum of sodium azide 100 mM in H_2O was obtained at 300 K with a Bruker Avance I (DRX-500, 300 K) NMR 11.7 T spectrometer. The spectrum was obtained in 30 s with 64 scans. The assignment of the peaks to the azide molecule and reference standard CH_3NO_2 are shown in Figure 5 (Magnetic Resonance Unit, University of Santiago de Compostela).

Superimposition of two spectra of sodium azide titrated with fullerene are shown in Figure 2. ^{14}N NMR titration study of C_{60} fullerene added to 1 M NaN_3 water solution. The black line corresponds to the molar ratio of sodium azide to C_{60} , which equals 10:1 in the water solution, while the green line corresponds to sodium azide titrated with the fullerene water solution at the lowest concentration of 0.38:1.

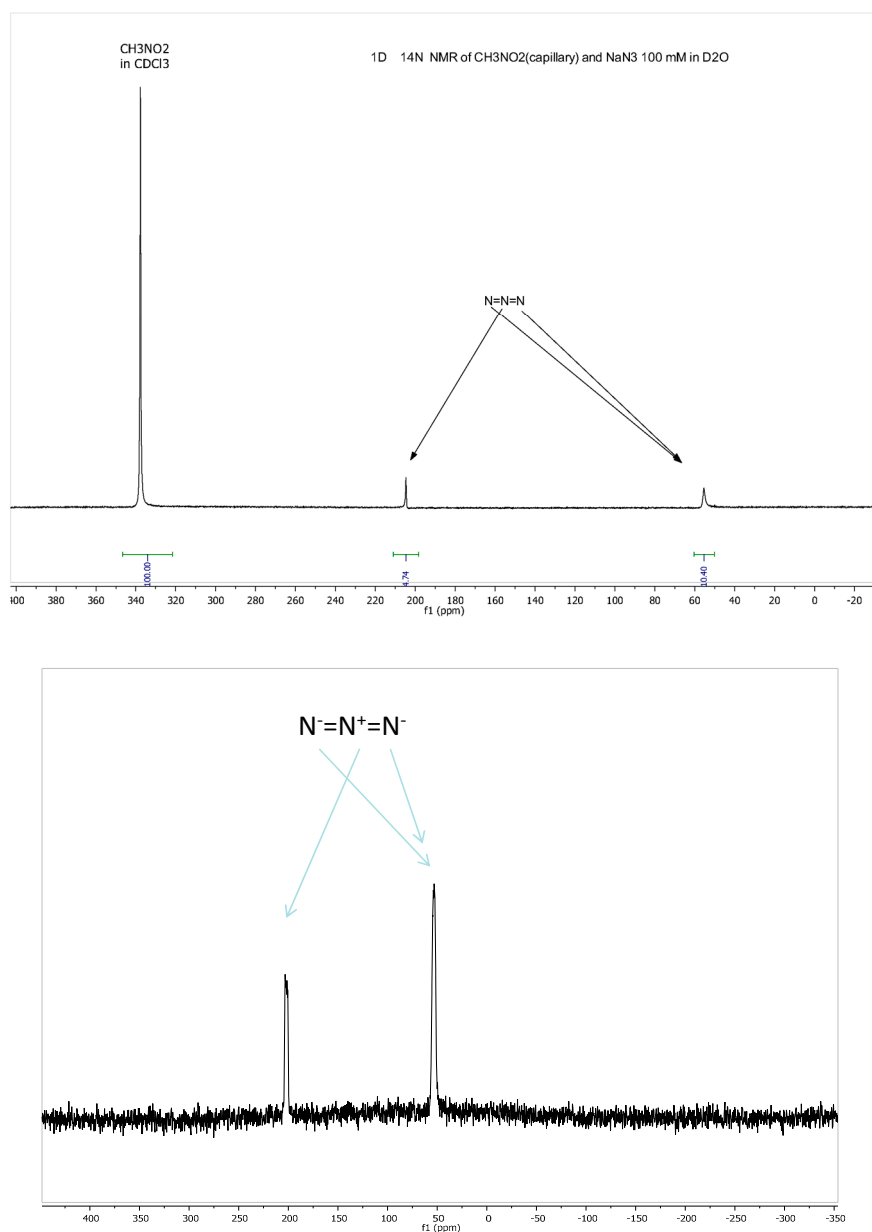


Figure 5. ^{14}N NMR spectrum of 100% CH_3NO_2 and 100 mM Sodium azide (NaN_3 in D_2O).

Measurements of the ^{14}N NMR spectrum were performed on a sample containing only sodium azide in water at the same concentration of 10 M to discard a false positive (Figure 6). Sodium azide is a highly soluble reagent i.e., $>10,000$ mg/L [31]. The solubility of sodium azide in water was reported to be 415 g/L, consistent at 20 °C [32].

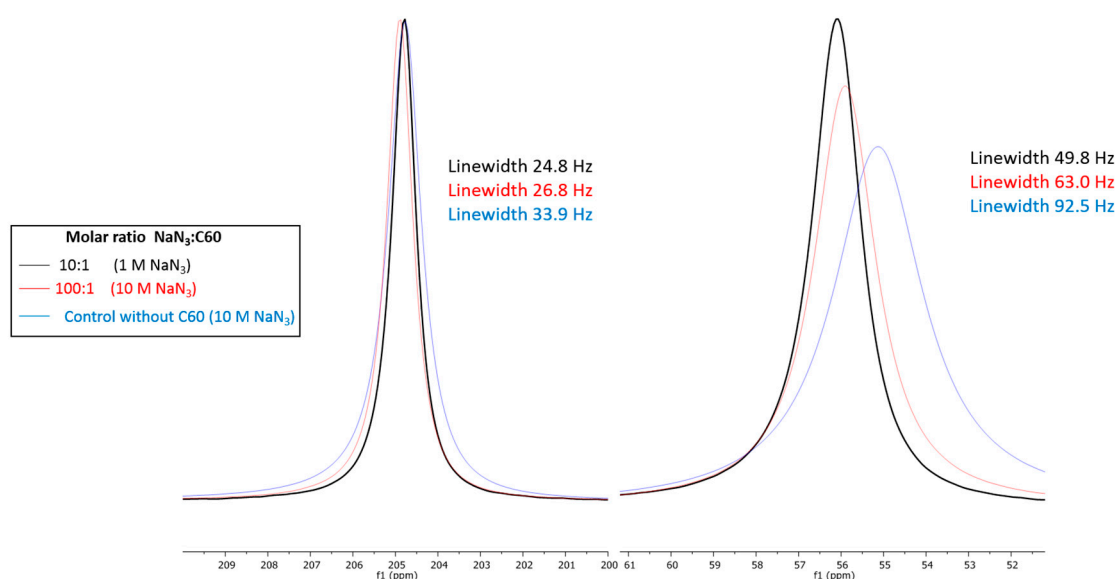


Figure 6. At a high molar ratio $\text{NaN}_3:\text{C60}$ ($>10:1$), there are some subtle changes in the ^{14}N NMR chemical shift and line-width of both NaN_3 peaks.

The sample prepared at a molar ratio of $\text{NaN}_3:\text{C60}$, 100:1 shows a small change in the peak position and as well as a change in the line-width with respect to the other samples explored in the titration study. These changes could be indicative of a weak binding interaction between NaN_3 and C60.

The ^{14}N peaks of sodium azide have observable chemical shift perturbations (CSPs) and changes in the line-width at all concentrations (Figure 7). These two effects are stronger for the two external nitrogen atoms of sodium azide (Signal B) than for the central nitrogen (Signal A). The abovementioned effects could indicate a weak binding interaction between NaN_3 and C60.

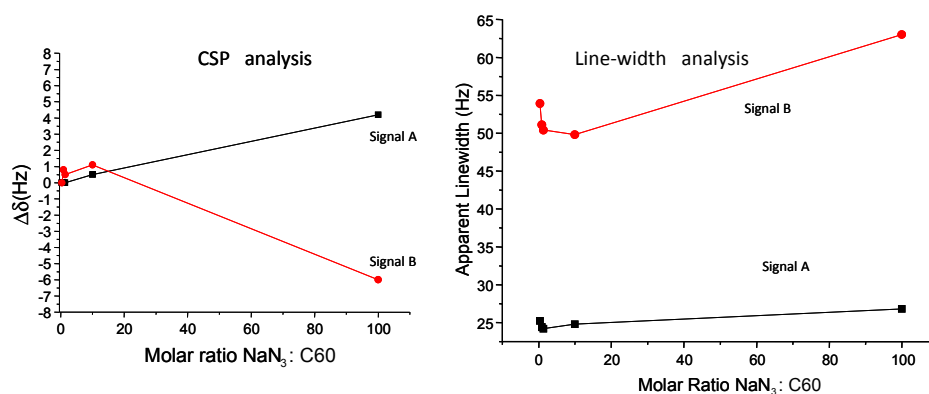


Figure 7. Chemical shift perturbations (CSPs) and line-width study of ^{14}N peaks of NaN_3 at several molar ratios.

Chemical shifts are very sensitive to the electronic environment of a nucleus. Perturbations in the chemical shift can be caused not only by a change in the covalent molecular structure, but also through non-covalent interactions with solvent molecules or binding partners. This makes chemical shifts a very sensitive probe for the identification of interaction surfaces in complexes.

Chemical shift mapping is suited to weak interactions in the <10 M range, giving rise to fast exchanges. In this situation, the chemical shifts reveal continuous changes along with the addition of the binding compound. The interaction is so weak that the complex only exists for part of the time

that takes to record the NMR experiment. The observed chemical shift is therefore a weighted average of the chemical shifts for C60 and the 10 M concentration of sodium azide, until the former has been added in excess.

Chemical shift mapping is a very straightforward method and can provide information about both the location and strength of a binding event to detect a weak binding between C60 and NaN₃.

4. Discussion

The results obtained demonstrate that there are changes in the chemical shift position and line-broadening related to the molar ratio of 10:1 and up to 100:1 of NaN₃:C60 in the samples.

These results can be interpreted as a binding interaction occurring between NaN₃ and C60 molecules. From the two observed ¹⁴N peaks of NaN₃, it can be concluded that the one more affected is that which resonates at approximately 56 ppm.

In the instant that the two molecules are bound their atoms are packed together and, as a consequence, their electron clouds introduce a slight shielding/de-shielding of the external magnetic field that can be felt by the nuclei of either of the two molecules. Thus, the ¹⁴N NMR peaks of the N₃ molecule appear to be, on average, in a slightly different magnetic field when C60 is present, and therefore the molecules resonate at a slightly different chemical shift compared to when C60 is not present. We conducted a titration with C60 and followed the changes in the chemical shifts of ¹⁴N. The fact that changes were observed at the addition of C60 demonstrates that the two molecules interact and bind together dynamically.

The influence of C60 in the chemical shifts of NaN₃ is not linear with the concentration, i.e., the two molecules interact in a one to one proportion as indicated above; they therefore have a quadratic dependence with the concentration.

It is known that fullerenes can be functionalized through chemical synthesis, by attaching different substituents (–COOR, OR, etc.) to the fullerene. C60 is like any electron-deficient molecule, and can accept from 1 to 6 electrons before C60 is converted into an anion. In the role of a donor, it will serve an external electrical charge, such as alkali metal ions or organic molecules.

Like alkenes, fullerene could be involved in the reaction of azide-alkyne cycloaddition, with the formation of triazole rings [33].

Azides are dipoles and have ambiphilic nature, which means that they can react with electrophiles and nucleophiles at the same time. Carbon-carbon bond distances are frequently used to describe and predict the regioselectivity of a reaction on a fullerene compound. The C60 molecule has two bond lengths. The 6:6 ring bonds (between two hexagons) can be considered “double bonds” and are shorter than the 6:5 bonds (between a hexagon and a pentagon). Its average bond length is 1.4 angstroms. 6–6 Bonds present the shortest bond distances as a result of the higher electronic density, on the other hand, 5–6 bonds are usually larger. Shorter C–C bond distances are in principle associated with enhanced reactivity, as they exhibit more double bond characteristics that facilitate interactions with dipoles [34]. Reactions with 6–6 bonds of fullerene are nucleophilic in nature, and it is the property which allowed for a non-chemical interaction to take place between C60 and NaN₃.

5. Conclusions

The results demonstrate that there are changes in the chemical shift positions and line-broadening which are related to the different molar ratios of NaN₃:C60 in the samples (<100:1). One of two peaks of ¹⁴N, which resonates at 56 ppm and corresponds to two external nitrogen atoms of NaN₃, is more affected by the influence of hydrated fullerene C60. These results can be interpreted as the indication of the weak binding interaction occurring between NaN₃ and C60 molecules.

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References

1. Petrović, M.; Gonzalez, S.; Barceló, D. Analysis and removal of emerging contaminants in wastewater and drinking water. *TrAC Trends Anal. Chem.* **2003**, *22*, 685–696. [[CrossRef](#)]
2. Focazio, M.J.; Kolpin, D.W.; Barnes, K.K.; Furlong, E.T.; Meyer, M.T.; Zaugg, S.D.; Thurman, M.E. A national reconnaissance for pharmaceuticals and other organic wastewater contaminants in the United States—II) Untreated drinking water sources. *Sci. Total Environ.* **2008**, *402*, 201–216. [[CrossRef](#)] [[PubMed](#)]
3. Buser, H.R.; Poiger, T.; Müller, M.D. Occurrence and environmental behavior of the chiral pharmaceutical drug ibuprofen in surface waters and in wastewater. *Environ. Sci. Technol.* **1999**, *33*, 2529–2535. [[CrossRef](#)]
4. Heberer, T. Occurrence, fate, and removal of pharmaceutical residues in the aquatic environment: A review of recent research data. *Toxicol. Lett.* **2002**, *131*, 5–17. [[CrossRef](#)]
5. Ternes, T.A. Occurrence of drugs in German sewage treatment plants and rivers. *Water Res.* **1998**, *32*, 3245–3260. [[CrossRef](#)]
6. Metcalfe, C.D.; Koenig, B.G.; Bennie, D.T.; Servos, M.; Ternes, T.A.; Hirsch, R. Occurrence of neutral and acidic drugs in the effluents of Canadian sewage treatment plants. *Environ. Toxicol. Chem.* **2003**, *22*, 2872–2880. [[CrossRef](#)] [[PubMed](#)]
7. Castiglioni, S.; Bagnati, R.; Fanelli, R.; Pomati, F.; Calamari, D.; Zuccato, E. Removal of pharmaceuticals in sewage treatment plants in Italy. *Environ. Sci. Technol.* **2006**, *40*, 357–363. [[CrossRef](#)] [[PubMed](#)]
8. Joss, A.; Keller, E.; Alder, A.C.; Göbel, A.; McArdell, C.S.; Ternes, T.; Siegrist, H. Removal of pharmaceuticals and fragrances in biological wastewater treatment. *Water Res.* **2005**, *39*, 3139–3152. [[CrossRef](#)] [[PubMed](#)]
9. Giger, W.; Alder, A.C.; Golet, E.M.; Kohler, H.P.E.; McArdell, C.S.; Molnar, E.; Suter, M.J.F. Occurrence and fate of antibiotics as trace contaminants in wastewaters, sewage sludges, and surface waters. *CHIMIA Int. J. Chem.* **2003**, *57*, 485–491. [[CrossRef](#)]
10. McKean, S. (Ed.) High Production Volume (HPV) Chemicals. In *The Organization for Economic Co-Operation and Development*; Environment Directorate: Paris, France, 2010.
11. Rodríguez-Kábana, R.; Robertson, D.G. Nematicidal and herbicidal properties of potassium azide. *Nematropica* **2000**, *30*, 146–147.
12. Wells, S. Granular Forms of Sodium and Potassium Azide as a Nematicide for Established Turfgrasses. Ph.D. Thesis, Auburn University, Auburn, AL, USA, 2009.
13. Betterton, E.A. Environmental fate of sodium azide derived from automobile airbags. *Crit. Rev. Environ. Sci. Technol.* **2003**, *33*, 423–458. [[CrossRef](#)]
14. Haase, J.; Banert, K. Large-scale preparation and usage of azides. In *Organic Azides: Syntheses and Applications*; John Wiley & Sons: Hoboken, NJ, USA, 2011.
15. Use of Dendrimers to Enhance Selective Separation of Nanofiltration and Reverse Osmosis Membranes. Available online: <https://www.usbr.gov/research/dwpr/reportpdfs/report140.pdf> (accessed on 1 February 2017).
16. Velizarov, S.; Crespo, J.G.; Reis, M.A. Removal of inorganic anions from drinking water supplies by membrane bio/processes. *Rev. Environ. Sci. Bio/Technol.* **2004**, *3*, 361–380. [[CrossRef](#)]
17. Park, H.; Chang, I.; Lee, K. Membranes and Module Modification. In *Principles of Membrane Bioreactors for Wastewater Treatment*; CRC press Taylor & Francis Group: New York, NY, USA, 2015; pp. 281–282.
18. Liu, Z.H.; Ogejo, J.A.; Pruden, A.; Knowlton, K.F. Occurrence, fate and removal of synthetic oral contraceptives (SOCs) in the natural environment: A review. *Sci. Total Environ.* **2011**, *409*, 5149–5161. [[CrossRef](#)] [[PubMed](#)]
19. Jassby, D.; Chae, S.R.; Hendren, Z.; Wiesner, M. Membrane filtration of fullerene nanoparticle suspensions: Effects of derivatization, pressure, electrolyte species and concentration. *J. Colloid Interface Sci.* **2010**, *346*, 296–302. [[CrossRef](#)] [[PubMed](#)]
20. Chae, S.R.; Therezien, M.; Budarz, J.F.; Wessel, L.; Lin, S.; Xiao, Y.; Wiesner, M.R. Comparison of the photosensitivity and bacterial toxicity of spherical and tubular fullerenes of variable aggregate size. *J. Nanopart. Res.* **2011**, *13*, 5121–5127. [[CrossRef](#)]

21. Jassby, D.; Chae, S.R.; Hendren, Z.; Wiesner, M.R. Membrane filtration of fullerene nanoparticle suspensions: Effects of derivatization, pressure and electrolyte concentration. *J. Colloid Interface Sci.* **2010**, *346*, 296–302. [[CrossRef](#)] [[PubMed](#)]
22. Chae, S.R.; Hotze, E.M.; Wiesner, M.R. Possible Applications of Fullerene Nanomaterials in Water Treatment and Reuse. In *Nanotechnology Applications for Clean Water*; William Andrew Publishing: Norwich, NY, USA, 2008.
23. Chae, S.R.; Wang, S.; Hendren, Z.D.; Wiesner, M.R.; Watanabe, Y.; Gunsch, C.K. Effects of fullerene nanoparticles on Escherichia coli K12 respiratory activity in aqueous suspension and potential use for membrane biofouling control. *J. Membr. Sci.* **2009**, *329*, 68–74. [[CrossRef](#)]
24. Jones, O.A.H.; Voulvoulis, N.; Lester, J.N. Human pharmaceuticals in wastewater treatment processes. *Crit. Rev. Environ. Sci. Technol.* **2005**, *35*, 401–427. [[CrossRef](#)]
25. Buseck, P.S.; Tsipursky, R.; Hettich, R. Fullerenes from the geological environment. *Science* **1992**, *257*, 215–217. [[CrossRef](#)] [[PubMed](#)]
26. Krasnovyd, S.V.; Konchits, A.A.; Shanina, B.D.; Valakh, M.Y.; Yanchuk, I.B.; Yukhymchuk, V.O.; Skoryk, M.A. Local structure and paramagnetic properties of the nanostructured carbonaceous material shungite. *Nanoscale Res. Lett.* **2015**, *10*, 78. [[CrossRef](#)] [[PubMed](#)]
27. Buseck, P.R. Geological fullerenes: Review and analysis. *Earth Planet. Sci. Lett.* **2002**, *203*, 781–792. [[CrossRef](#)]
28. Augustyniak-Jabłokow, M.A.; Yablokov, Y.V.; Andrzejewski, B.; Kempieński, W.; Łoś, S.; Tadzysak, K.; Zhikharev, V.A. EPR and magnetism of the nanostructured natural carbonaceous material shungite. *Phys. Chem. Miner.* **2010**, *37*, 237–247. [[CrossRef](#)]
29. Andrievsky, G.V.; Kosevich, M.V.; Vovk, M.; Shelkovsky, V.S.; Vashchenko, L.A. On the production of an aqueous colloidal solution of fullerenes. *J. Chem. Soc. Chem. Commun.* **1995**, *12*, 1281–1282. [[CrossRef](#)]
30. Chachibaia, T.; Pastor, M. The State-Of-The-Art chemical analytical method for detection of sodium azide by ¹⁴N NMR spectroscopy. *J. Nano Stud.* **2015**, *11*, 8–15.
31. Krebs, F. Determination of the Biological Harmful Effects of Substances Endangering Water Quality with the Assimilation-Depletion Test (A-D Test). *Deutsche Gewässerkundliche Mitteilungen* **1991**, *35*, 161–170.
32. O'Neill, M.J. (Ed.) *Sodium Azide, The Merck Index, an Encyclopedia of Hemicals, Drugs, and Biologicals*, 14th ed.; RSC Publishing: Cambridge, UK, 2006; pp. 1478–1479.
33. Akhmetov, A.R.; Tuktarov, A.R.; Dzhemilev, U.M.; Yarullin, I.R.; Gabidullina, L.A. First example of the interaction of fullerene C₆₀ with hydrazoic acid. *Rus. Chem. Bull.* **2011**, *60*, 1885–1887. [[CrossRef](#)]
34. Osuna Oliveras, S. Theoretical Studies of the Exohedral Reactivity of Fullerene Compounds. Ph.D. Thesis, Universitat de Girona, Girona, Spain, 2010.

