We show that large fullerenes (LFs) are soluble in concentrated sulfuric acids. We employ a centrifugation technique in conjunction with ultraviolet-visible and near-infrared (UV-vis-nIR) spectroscopy to quantify solubility. The Beer’s Law dependence of UV-vis-nIR absorbance of LFs in concentrated sulfuric acids between 400 and 1400 nm facilitates the construction of linear calibration curves for measuring LF concentration in acids. Centrifugation of concentrated dispersions of LFs in concentrated sulfuric acids results in a clear phase separation. UV-vis-nIR absorbance measurements on the less concentrated phase yield the solubility of LFs. Large fullerenes exhibit an unusually high solubility in sulfuric acids concentrated in the range of 88–96%. The solubility of LFs in 96% sulfuric acid is higher than the solubility of the smallest fullerene (C_{60}) in many organic solvents. We find that the solubility of LFs grows with acid strength, as is expected for solubilization by a protonation mechanism. Moreover, the average size of LFs solubilized in sulfuric acid increases with the strength of the acid.

1. Introduction

Since the discovery of fullerenes by Smalley and co-workers,1 the physical and chemical properties of C_{60} and C_{70} fullerenes have been widely investigated. Fullerenes represent a unique category of cage molecules with a wide range of sizes, shapes, and molecular weights.2 The potential for applications in material sciences3,4 such as superconductors,5,6 batteries, catalysts, or novel optical devices,7,8 or in organic or pharmaceutical chemistry9 is enhanced by the possibility of producing fullerenes of different sizes and shapes. Besides the relatively well-known C_{60} and C_{70} fullerenes, a large class of so-called “fullerenic” compounds such as nanotubes14 or onion-like nanostructures15 have been identified and investigated. Fullerene chemistry continues to be an exciting field; many articles are published every year with advances in basic science and promising applications.16,17

2. Methods and Discussion

Fullerenes have limited solubility in common solvents. Ruoff and co-workers18 investigated the temperature-dependent solubility of C_{60} in hexane and toluene; comprehensive lists of solubility of C_{60} in various solvents can be found in refs 19–21 and references therein. Fullerenes themselves are virtually insoluble in water;22 potential applications in biology and medicine have motivated attempts to make water-stable systems. Limited water solubility of fullerenes has been achieved by chemical modification,23,24–26 formation of water-soluble host–guest complexes,27,28 or solubilization by surfactants.28–29 Specifically, C_{60} fullerene has been made soluble by connecting it with functional chargeable groups such as carboxylic acids30–32 amines33,34 or phenyl groups.35–37 Deguchi et al.38 reported stable aqueous dispersions of C_{60} and C_{70} prepared by injecting a saturated solution of fullerene in tetrahydrofuran (THF) into water, followed by THF removal by purging with gaseous nitrogen.

Though smaller fullerenes, such as C_{60}, C_{70}, C_{76}, and C_{84}, have been widely studied, less is known about the characterization and processing of large fullerenes (LFs, >C_{100}). Most studies on LFs are concentrated on molecular mechanics calculations of shape, size, and geometry,39–42 and electronic structure.43,44 Macroscopic characterization by IR, Raman, nuclear magnetic resonance (NMR), X-ray diffraction (XRD), and transmission electron microscopy (TEM) is rarely reported45 as are the identification and extraction of LFs.46–48

The studies most relevant to the work described here are those of Cataldo49 and Reed et al.,50 who report stabilization of fullerenes through the use of superacids. Cataldo50 report that oleum oxidizes C_{60} with free SO_{3}, leading to the formation of C_{60} cations. Chiang and co-workers51–53 have also reported polycyclosulfation of C_{60} with fuming sulfuric acid (28–30 wt % excess SO_{3}). Similar findings are also reported by Kukolich and Huffman.54 Reed et al.50 report reaction of the superacid H(CB_{11}H_{6}X)_{6} (where X = chlorine or bromine) with C_{60} to give HC_{60}X^+ as a stable ion in solution and in the solid state. The protonation of C_{60} is reversible. Exposure of the solution to a base via aerobic moisture or by the addition of Na_{2}CO_{3}(s) returns the spectrum to that of C_{60}. To the best of our knowledge, however, the solubility of LFs in any solvent has never been reported. Here, we report the unusually high solubility of LFs in concentrated sulfuric acids (64–96% H_{2}SO_{4}) and a convenient route to separate LFs by size.

Our technique for quantifying the solubility of LFs in concentrated sulfuric acids relies on centrifugation in conjunction with a method for measuring the concentration of dispersions.
of LFs in acids by UV−vis−nIR spectroscopy. A higher-order fullerene mixture was acquired from the Materials and Electrochemical Research (MER) Corporation (Tucson, Arizona). Smaller fullerenes (C_{60} and C_{70}) were removed from this mixture by dissolving them in ortho-dichlorobenzene, because the orthodichlorobenzene has one of the highest solubilities for C_{60}. A matrix-assisted laser desorption ionization (MALDI) mass spectrum proves that this material is fullerenic (see Figure 4a and also Supporting Information). The raw sample shows a mass spectral span of 1200−4500 amu with the maximal intensity at 1850 amu. The masses were evenly separated at a spacing of 24 amu, a well-known feature in the mass spectral pattern of fullerenes arising from the loss of C_{2} species. The MALDI spectrum also shows the absence of small fullerenes such as C_{60} or C_{70} in the starting material. Figure 1 is a TEM image of the starting material showing that it consists of mostly LFs. Lighter fullerenes such as C_{60} or C_{70} and carbon nanotubes are present in very small quantities in the starting material, if at all. Thermogravimetric analysis (TGA) shows that metal content of the sample is less than 2 wt %. ACS-certified 96% sulfuric acid was purchased from Sigma Aldrich and was used as received without purification. Lower concentrations of sulfuric acid were prepared by slowly adding water to 96% sulfuric acid and mixing with a magnetic stirrer. LF dispersions were prepared by gentle mixing with a magnetic stir bar (no sonication) for a minimum of 72 h at room temperature in an anhydrous environment (a glovebox with a dewpoint of −50 °C) to prevent moisture ingress. After mixing, the samples were centrifuged on a Fisher Centrifuge model 225 benchtop centrifuge at 5100 rpm. UV−vis−nIR absorbance spectra were measured on a Shimadzu UV-3101PC spectrometer in 1 mm path-length Starna cells with Teflon closures. Elemental analysis of dissolved LFs was performed by X-ray photoelectron spectroscopy (XPS) on a PHI Quantera XPS.

At low concentrations of LFs in sulfuric acids, light absorbance in the range from 400 to 1400 nm scales linearly with concentration. This Beer’s Law behavior yields calibration curves for measuring LFs concentration in acids. Concentrated dispersions of LFs in concentrated sulfuric acids were centrifuged for 12 or more hours (after which no measurable changes in concentration could be detected in the centrifugation vials); phase separation was visible in the lower acidity samples. The lower absorbance of the fullerene dispersion in the dilute phase at all wavelengths shows that phase separation occurs during the process of centrifugation. The less concentrated phase was diluted with a known amount of solvent; UV−vis−nIR absorbance measurements provided a quantitative measurement of concentration.

Figure 2 shows photographs of vials of LFs centrifuged from a starting concentration of 1500 ppm (or 0.15 wt %) in different strengths of sulfuric acid (a) 96%, (b) 88%, (c) 84%, (d) 80%, and (e) 64%; these dispersions display various extents of phase separation upon extended centrifugation at 5100 rpm. A vial of 96% H_{2}SO_{4} (Figure 2f, shown for comparison) is a clear liquid. The phase separation of LFs from 64% H_{2}SO_{4} is almost complete; therefore, the solubility of LFs in 64% sulfuric acid is minimal. In 64% H_{2}SO_{4} (\rho_{64%} = 1.44, \rho_{l} = 1.65; where \rho_{64%} is the density of the 64% sulfuric acid and \rho_{l} is the density of the LFs) the top phase is structureless and optically uniform, whereas the bottom phase includes most of the fullerenes. In 80−84% sulfuric acid (\rho_{80%} = 1.73 and \rho_{84%} = 1.77), where the density of the fullerenes is only slightly lower than that of the solvent, phase separation of fullerenes is visible upon centrifugation; most of the LFs cream at the top. However, the acid has acquired some coloration, indicating that some of the LFs have dissolved. Some particles are visible in the dilute phase. These are due to the minimal difference in density between LFs and 80−84% sulfuric acid; removing the vials from the centrifuge causes some of the top to diffuse. In 88% H_{2}SO_{4} (\rho_{88%} = 1.80), the initial dispersion of LFs, upon centrifugation, separates into a low concentration supernatant solution and a concentrated flocculated suspension of fullerenes in acid at the bottom. This phase separation is not obvious in the photographic image in Figure 2 because of the high solubility of LFs in 88% H_{2}SO_{4}, but it is clear from microscopic observation and UV−vis−nIR measurements. It is surprising that the LF-rich phase would be at the top in 80−84% sulfuric acid and at the bottom in 88% acid because the density of the acid grows with SO_{3} content. This behavior is similar to that of single-walled carbon nanotubes in sulfuric acids, where the protonated nanotubes associate with ordered sulfuric acid into a higher-density mixture. In 96% H_{2}SO_{4} (\rho = 1.84), the dispersion is fully stable, and no phase separation occurs over 48 h of continuous centrifugation. On the basis of the analysis of Holladay and the relative densities of LFs and 96% sulfuric acid, we estimate that particles above ~5 nm would separate under the centrifugation conditions. This suggests that, in 96% H_{2}SO_{4}, the LFs are present as individuals (i.e., their solubility is higher than 1500
Sulfur trioxide first attacks the fullerenes. Similar findings are also reported by Kukolich and Huffman. Polycyclosulfated fullerenes are reported to precipitate out from the acid solution as orange-red solids. Because our acid dispersion of LFs had neither SO$_3$ nor any solid precipitation, we believe that LFs are not functionalized but are truly soluble in concentrated sulfuric acids. We further checked that LFs are not functionalized by performing XPS. XPS identifies elements from lithium to uranium, with detection levels down to one atomic percent. If LFs are really functionalized in 96% sulfuric acid, then the XPS spectra should detect sulfur atoms. LFs were dissolved in 96% H$_2$SO$_4$ for two weeks and were subsequently quenched in ether and washed with methanol on a polycarbonate filter paper. The XPS spectra of these LFs (see Supporting Information) shows that the sample consists entirely of carbon atoms; the sulfur content is less than 0.1% (atomic), which is below the sensitivity of the instrument. This proves that LFs were not functionalized in concentrated sulfuric acids. We hypothesize that 96% H$_2$SO$_4$ is a strong enough acid to form a reversible polycarboxilation similar to what is observed in the case of single-walled carbon nanotubes in fuming sulfuric acid. Such fractional charge on the carbon atoms is sufficient to stabilize the LFs but is not strong enough to functionalize them. Interestingly, no metal was detected in the XPS spectra.

The size distribution of LFs solubilized in different strengths of sulfuric acid was measured by MALDI spectroscopy. Because acid-stabilized dispersions of fullerenes do not show any MALDI peaks characteristic of fullerenes, it was necessary to transfer fullerenes from acid into an organic solvent. Acid dispersions of fullerenes were quenched in nanopure water (15:1 excess water), soaked overnight, settled at the bottom of the vial by centrifuging for few minutes (~5 min), resuspended in nanopure water at least twice (to remove any residual acid), and then collected again at the bottom of the vial by centrifugation. Figure 4 shows the size distribution of LFs in the starting material and in those dissolved in sulfuric acid after quenching and washing with water. The mass spectra of the starting material shows the maximum intensity at 1850 amu. The mass spectra of LFs solubilized in 90% H$_2$SO$_4$ show the maximum intensity around 1450 amu and in 96% H$_2$SO$_4$ around 1700 amu, close to the starting material. This indicates that smaller LFs are solubilized preferentially in the weaker acids. This dependence of the size of solubilized LFs on the strength of sulfuric acid is consistent with the observation that even stronger acids (superacids) are needed to solubilize single-
walled carbon nanotubes. 35,62,63 The ability to separate LFs by size by varying the strength of the acid provides an important advancement that could be useful in various applications.

3. Conclusion

A centrifugation technique has been used in conjunction with UV-vis-nIR spectroscopy to quantify the solubility of large fullerenes in concentrated sulfuric acids (weaker than 96% H2SO4). Large fullerenes exhibit an unusually high solubility in the range of 88–96% H2SO4. The solubility of large fullerenes is higher than 10 000 ppm, or 1 wt %, in 96% H2SO4. Large fullerenes are not functionalized in these concentrated sulfuric acids; therefore, the dispersion mechanism is dissolution. The average size of LFs solubilized in sulfuric acid increases with the strength of the acid. This work opens the way to further understanding the mechanism of large fullerene stabilization in acid dispersions, which will be important for the extraction, isolation, and purification of large fullerenes.

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Supporting Information Available: MALDI spectra of large fullerenes in the starting material and XPS spectra of large fullerenes dissolve in 96% sulfuric acid for two weeks and then quenched in ether and washed with methanol. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(2) Dresselhaus, M. S. Nat. Mater. 2003, 2, 650.